Consortium for Advanced Battery Simulation (CABS)

Project ID: ES295

PI: John A. Turner

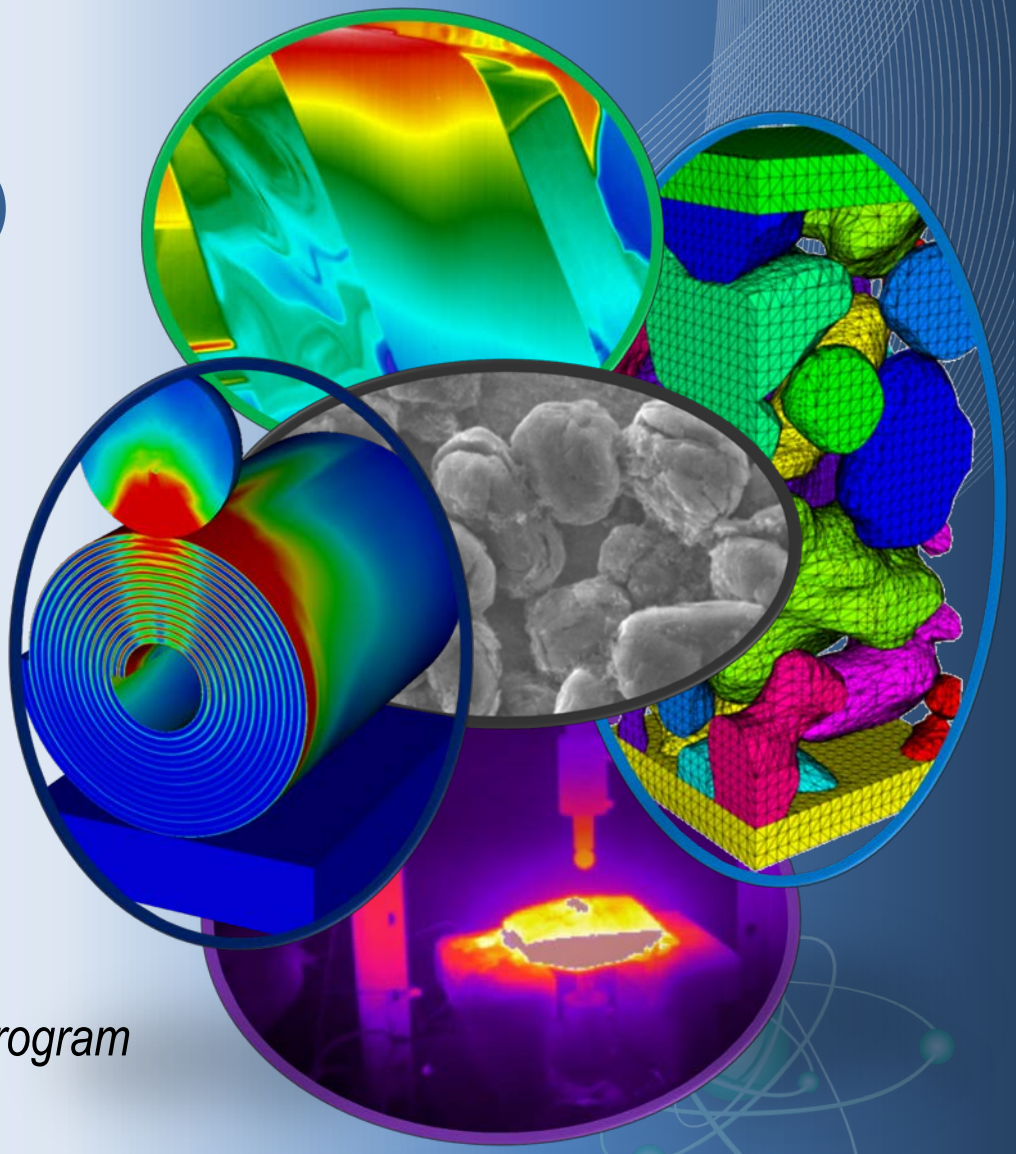
Team: Srikanth Allu, Wael Elwasif, Kenny Higa, Sergiy Kalnaus, Scott Roberts, Srdjan Simunovic, Venkat Srinivasan, Hsin Wang

June 7, 2015

2016 U.S. DOE Hydrogen and Vehicle Technologies Program

Annual Merit Review and Peer Evaluation

Brian Cunningham, Vehicle Technologies Program



This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start
  - October 2016
- Finish
  - September 2019
- Percent complete: 15

Barriers Addressed

Advanced simulation capabilities enable improved / optimized design, allowing the following barriers to be addressed:

C. Performance

D. Abuse Tolerance, Reliability, and Ruggedness

E. Life

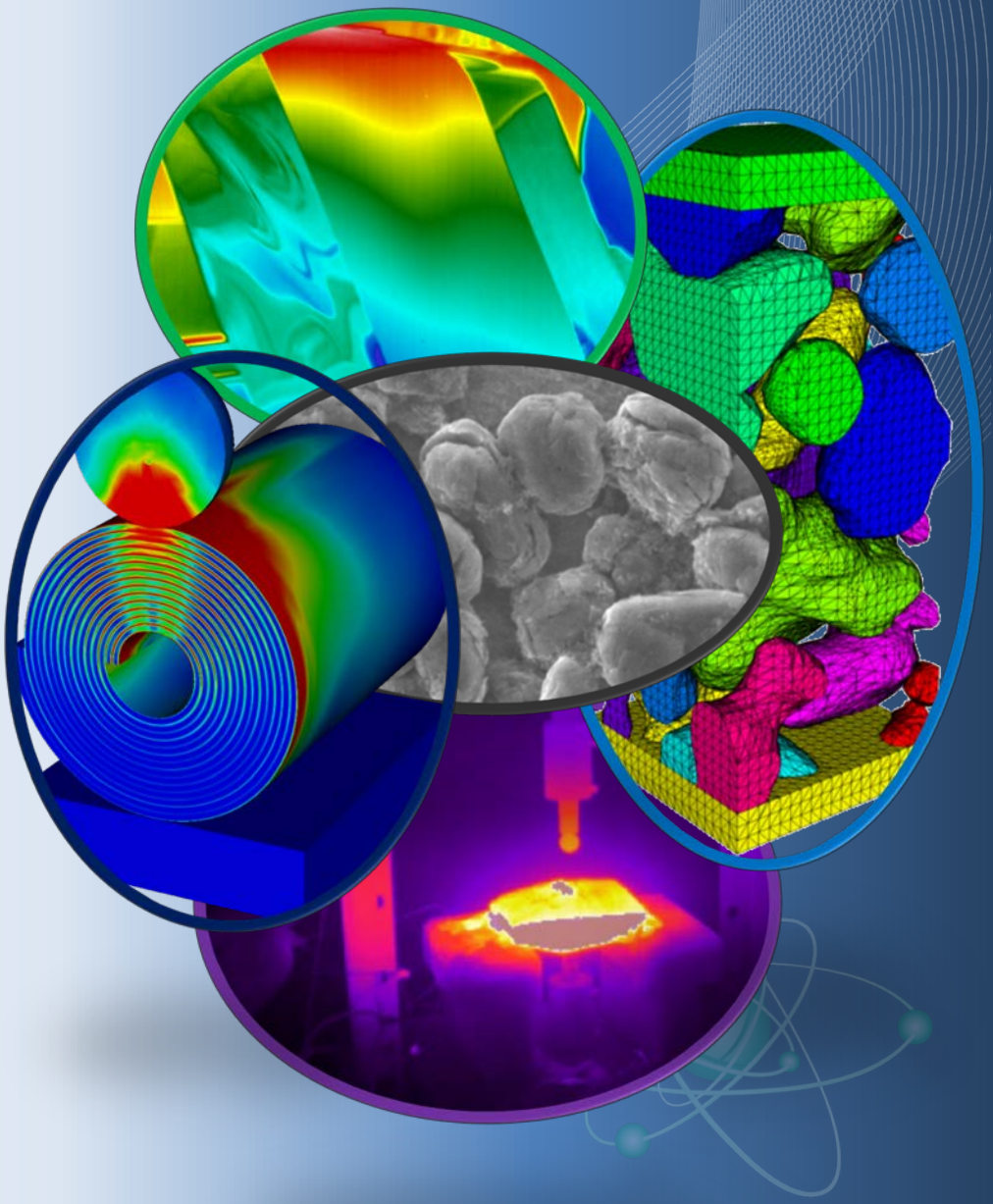
Budget

- FY16
  - $1.575M

Partners

- LBNL
- SNL
- as well as the NREL-led CAEBAT project team

Relevance



Relevance and Project Objectives (1)

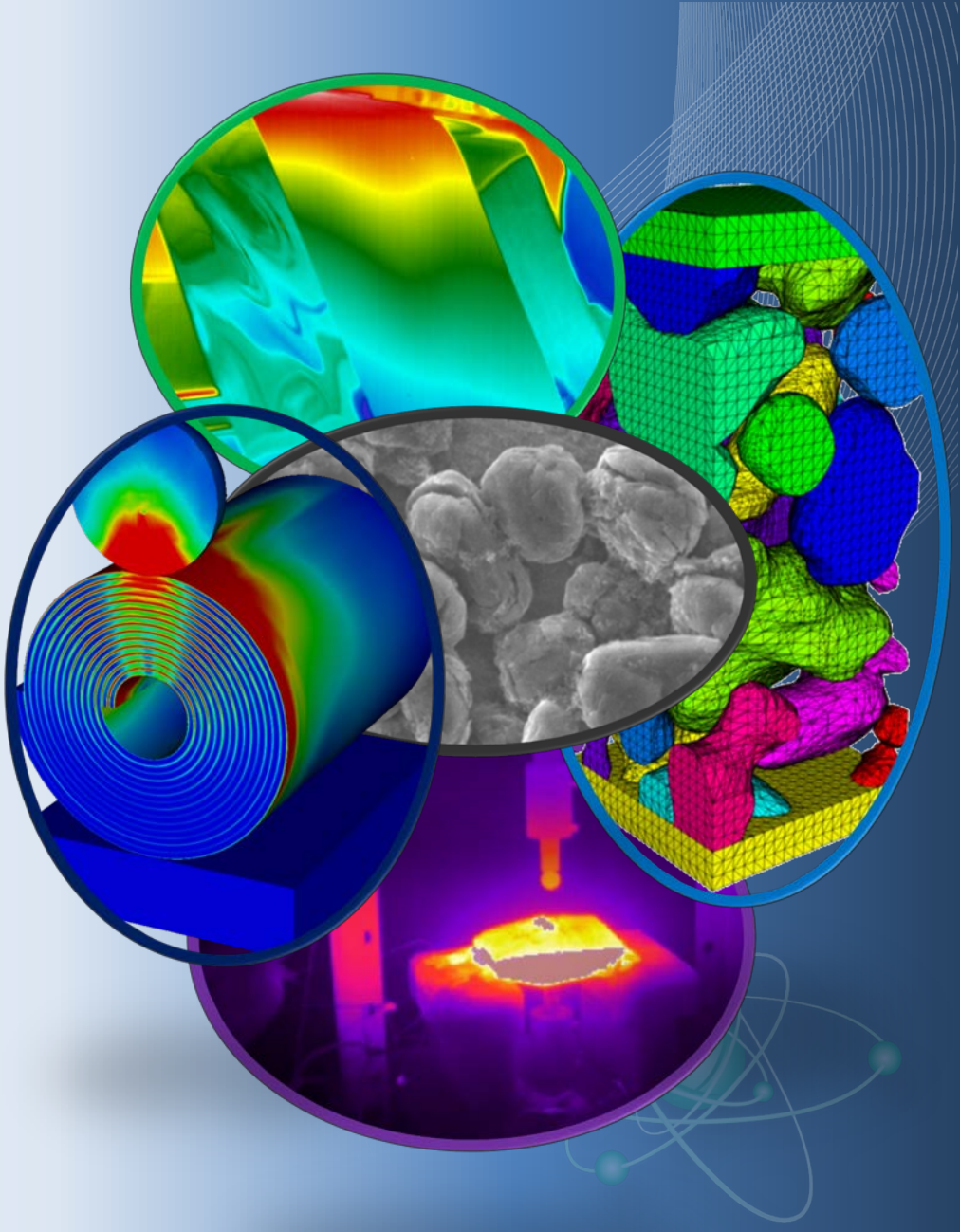
- Major barriers for increasing battery energy density and power, increasing safety and reducing cost include
  1. insufficient understanding of the underlying physical phenomena that limit battery performance and safety, particularly the role of microstructure, and
  2. lack of validated predictive simulation tools.
- CABS is addressing (1) by developing new experiments for properties with largest uncertainties and developing new validated models that allow researchers to explore battery response under both normal and abusive conditions, and is addressing (2) by deploying increasingly capable and computationally efficient releases of the Open Architecture Software (OAS) and components of the Virtual Integrated Battery Environment (VIBE), developed as part of CAEBAT 1.
- First released in Fall of 2014, VIBE has been downloaded over 100 times.

Relevance and Project Objectives (2)

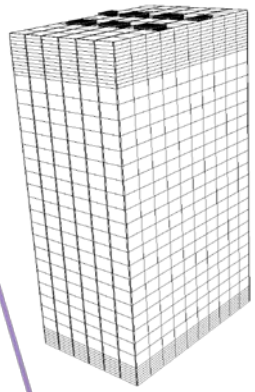
- CABS enables researchers and battery designers to explore and optimize batteries using new materials, configurations, and designs by
  - developing improved mechanistic models,
  - obtaining data from new and existing experiments, and
  - deploying successively more capable, efficient, and usable releases of VIBE
- This supports EERE's *EV Everywhere* goals by enabling increases in energy density, specific energy, and power while maintaining safety
  - Outcome: increased adoption of EVs
    - reduced emission of greenhouse gases
    - improved economic competitiveness of the U.S., in large part by reducing dependence on foreign oil.

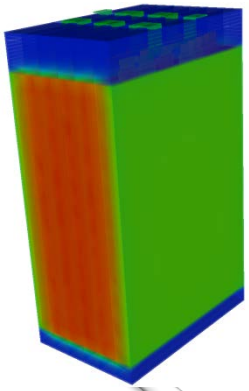
Approach / Strategy

High-level approach/strategy is shown in the following 3 slides, but is also embedded in the milestone slides within Technical Accomplishments.



Approach (1)





Pack

Efficient hybrid models

Constitutive models for electrode deformation

Constitutive and failure models for cells

Microstructure models

Homogenization methods

Criteria for internal short circuit

Models

Experiments

Mechanical Properties

Deformation

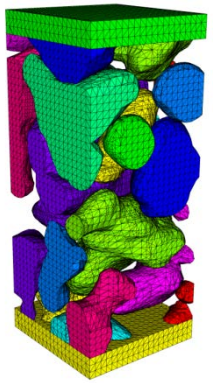
Thermal Properties

Electrochem. Performance

Imaging

Kinetic/Transport

Electrode



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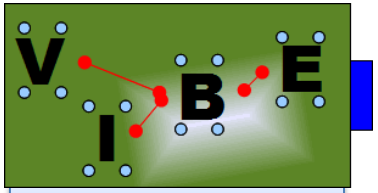
Approach (2)



Virtual Integrated Battery Environment **(VIBE)**

- Computational efficiency
  - Hybrid models
  - Software design – reducing file-based communication
  - State management library for OAS components
  - Continuous execution

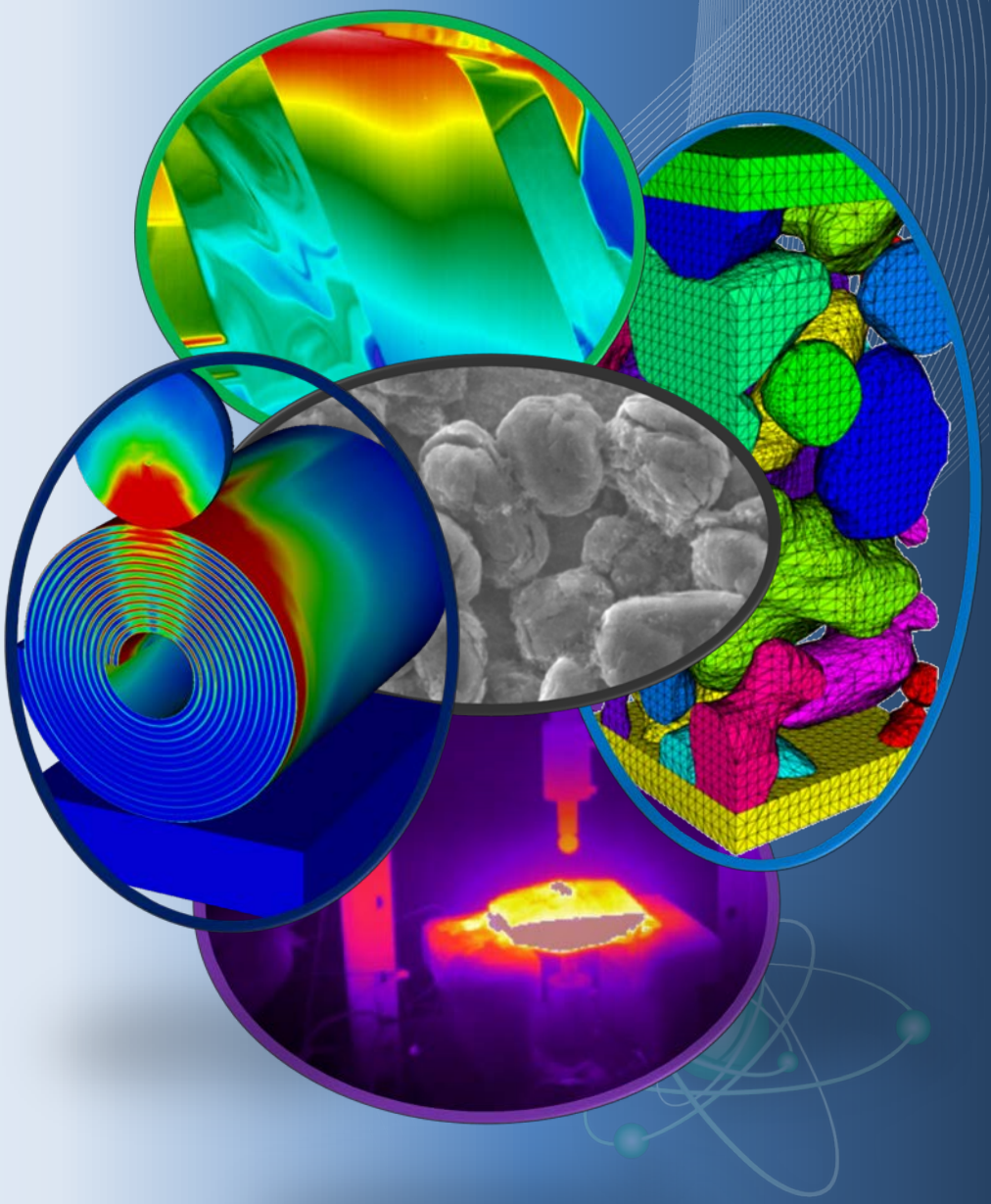
CABS FY16 Milestones

IDs indicate whether milestones are primarily experimental (E), computational (C), or integrated (I).							
ID	FY16	Lead	Q1	Q2	Q3	Q4	Status
C.1	Baseline performance profile of VIBE/OAS/AMPERES	ORNL	P				Complete
I.1	Report on experimental techniques supporting models	ORNL		P			Complete
E.1	Produce segmented tomographic reconstructions of electrodes for conversion to spatial domains for microstructural models	LBNL			P		On Track
E.2	Demonstration of single side indentation test with incremental deformation to determine faulting in spirally wound, wound prismatic, and stacked electrodes in hard case	ORNL				P	On Track
C1.1	Collect constitutive models for NMC materials and report on use of mesoscale data to project lead.	SNL				P	On Track
I.2	Deployment of VIBE/OAS with enhanced extensibility and hybrid models	ORNL				S	On Track

Technical Accomplishments

Includes:

- Foundation provided by previous CAEBAT projects and related efforts
- Summary of completed FY16 milestones, including approach



Technical Accomplishments

- The Virtual Integrated Battery Environment (VIBE) was developed under the initial CAEBAT program as a mechanism for demonstrating and deploying the Open Architecture Software (OAS) system used to foster interoperability between battery simulation tools.
- Although the earlier CAEBAT project ended in FY15, since CABS builds on that work, we include a brief overview of VIBE and selected accomplishments in the following slides.

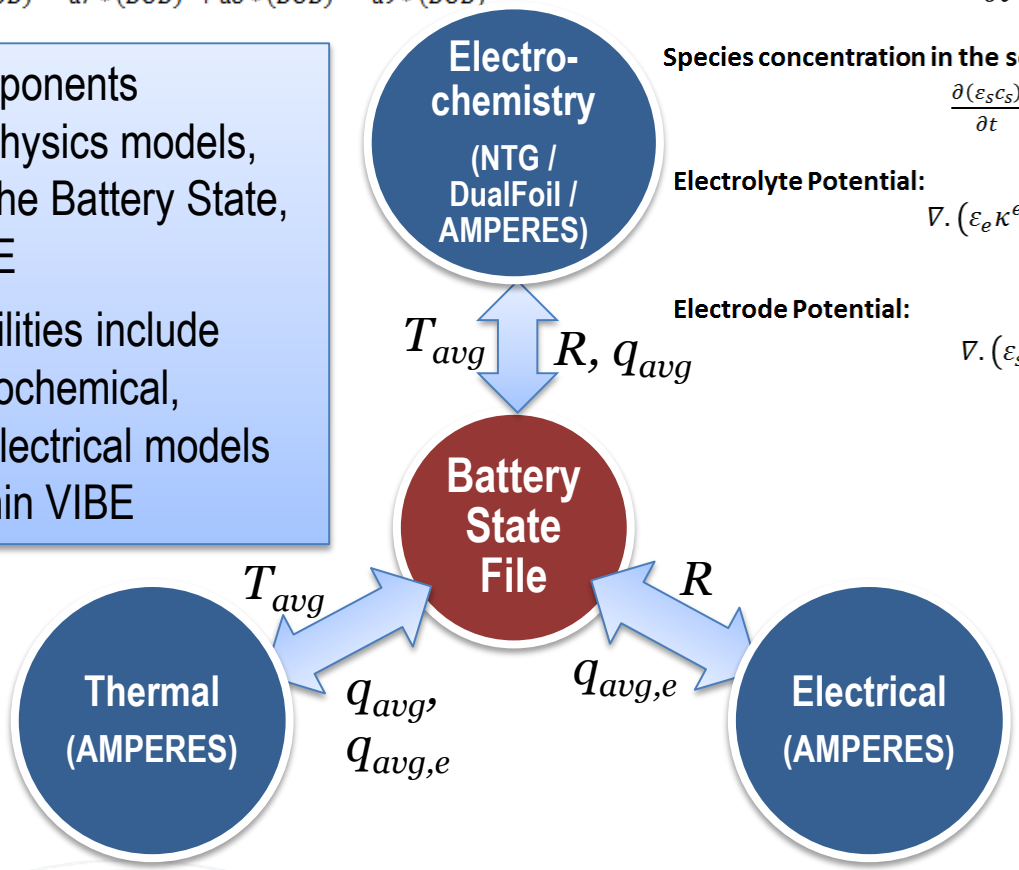
Virtual Integrated Battery Environment (VIBE)

$J = Y(Vp - Vn - U)$

$U = a0 + a1(DOD) + a2(DOD)^2 + a3(DOD)^3$

$Y = a4 - a5 * DOD + a6 * (DOD)^2 - a7 * (DOD)^3 + a8 * (DOD)^4 - a9 * (DOD)^5$

- OAS plus components representing physics models, together with the Battery State, constitute VIBE
- Current capabilities include coupled electrochemical, thermal, and electrical models integrated within VIBE



Species concentration in the electrolyte:

$$\frac{\partial(\varepsilon_e c_e)}{\partial t} - \nabla.\left(\varepsilon_e D_e^{eff}(\varepsilon_e)\nabla c_e\right) - \frac{1-t_+^0}{F} j^{Li} = 0$$

Species concentration in the solid phase:

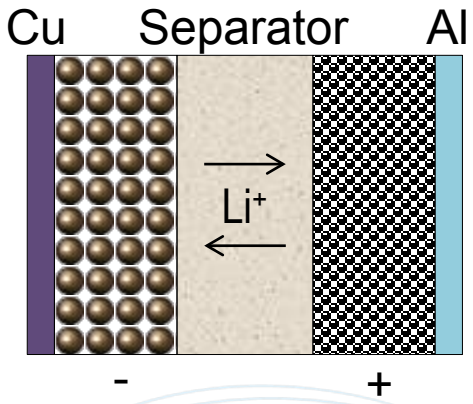
$$\frac{\partial(\varepsilon_s c_s)}{\partial t} - \nabla.\left(\varepsilon_s D_s^{eff}(\varepsilon_s)\nabla c_s\right) + \frac{j^{Li}}{F} = 0$$

Electrolyte Potential:

$$\nabla.\left(\varepsilon_e \kappa^{eff}(\varepsilon_e)\nabla\phi_e\right) + \nabla.\left(\varepsilon_e \kappa_D^{eff}(\varepsilon_e)\nabla \ln c_e\right) + j^{Li} = 0$$

Electrode Potential:

$$\nabla.\left(\varepsilon_s \sigma^{eff}(\varepsilon_s)\nabla\phi_s\right) - j^{Li} = 0$$



$$\rho Cp\frac{\partial T}{\partial t} - \frac{\partial}{\partial x}\left(kx\frac{\partial T}{\partial x}\right) - \frac{\partial}{\partial y}\left(ky\frac{\partial T}{\partial y}\right) - \frac{\partial}{\partial z}\left(kz\frac{\partial T}{\partial z}\right) = q$$

$$where \quad q = aJ\left[Eoc - E - T\frac{\partial Eoc}{\partial T}\right] + a_p\, r_p\, {i_p}^2 + a_n\, r_n\, {i_n}^2$$

Conservation of current flow:

$$\nabla \cdot \left(\frac{1}{r_p}\nabla V\right) = 0$$

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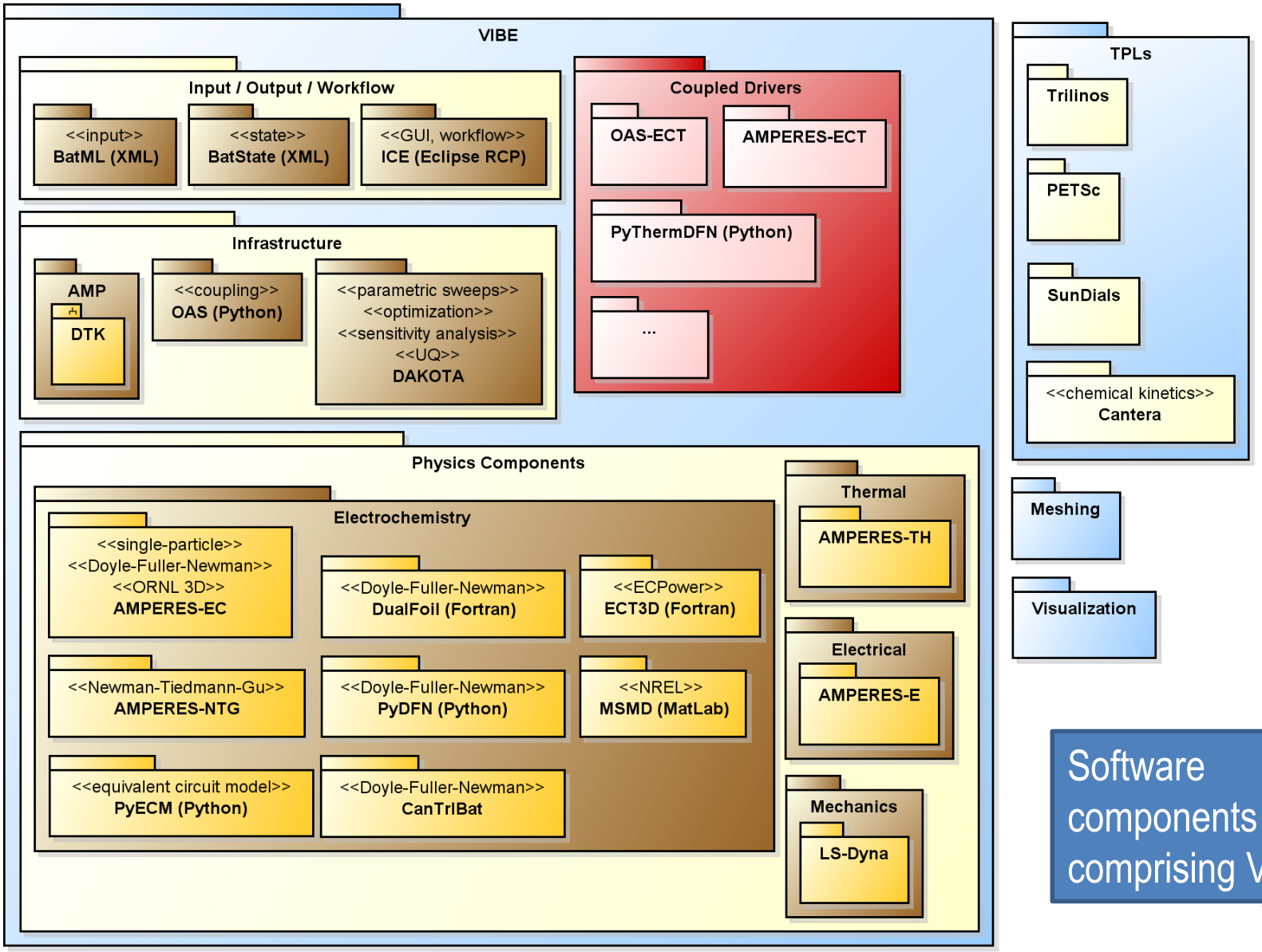
Virtual Integrated Battery Environment



Software components comprising VIBE.

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VIBE components have been coupled in multiple combinations depending on application need

- DualFoil electrochemistry + AMPERES thermal
- DualFoil electrochemistry + AMPERES thermal + AMPERES electrical
- AutoLion (ECPower) + Dakota (for optimization / parameter sweep)
- 1DElectrode electrochemistry (SNL) + AMPERES thermal
- 1DElectrode electrochemistry + AMPERES thermal + AMPERES electrical
- AMPERES NTG electrochemistry + AMPERES thermal
- AMPERES NTG electrochemistry + AMPERES thermal + AMPERES electrical
- AMPERES 3D electrochemistry + LS-Dyna mechanics

http://ecpowergroup.com/autolion-2/
https://dakota.sandia.gov/

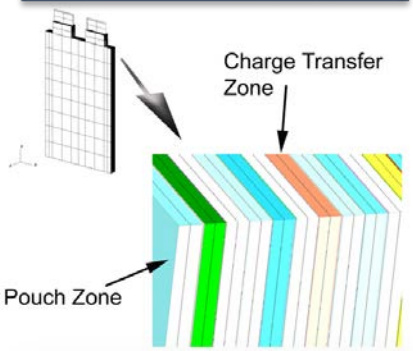
VIBE – Download Statistics

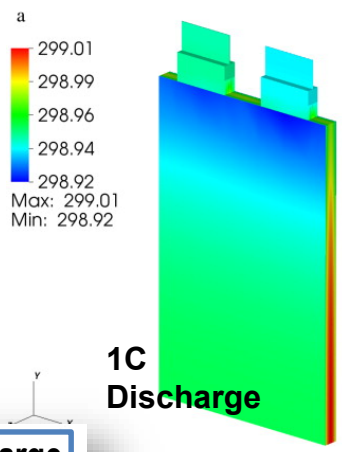
- >150 downloads via http://batterysim.org/
- Downloads from all over the world from labs, academia, and industry. Some of the institutions are listed below:

Apple	Fisker Automotive	Northeastern University
NASA	Texas A&M Univ.	Fiat Chrysler Automobiles
Lockheed Martin	Stanley Black & Decker	Georgia Tech
Ford Motor Company	BASF Corporation	Iowa State University
Bosch, LLC	Saft America	University of Maryland
Honda R&D Co, Ltd	Motorola	University of Michigan
Samsung Electronics	Pan Asia Technical Automotive Center	Purdue University
Virtual Vehicle Research Center	CEA – Commissariat Energie Atomique	North Carolina State University
Zee Aero	ICT Fraunhofer	University of Dayton
IK4-CIDETEC	Washington University	University of Nevada, Las Vegas
Institute for Energy and Environmental Research, Heidelberg, GmbH	TU Muenchen	SAIT Polytechnic

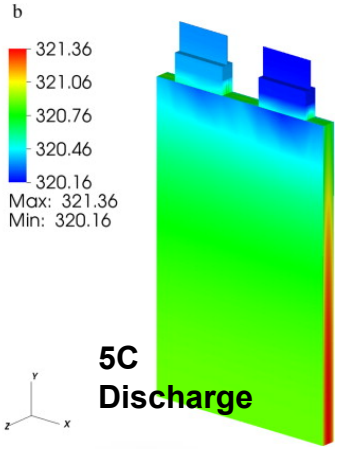
Overview of VIBE simulations

Detailed 3D Modeling

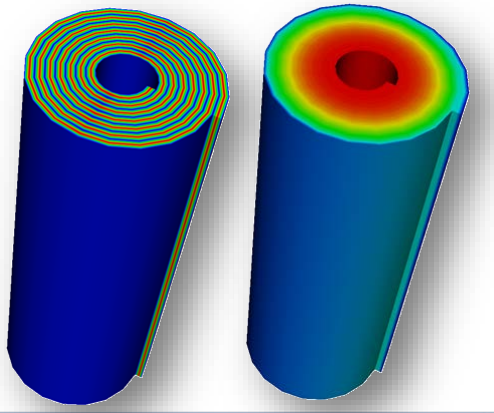




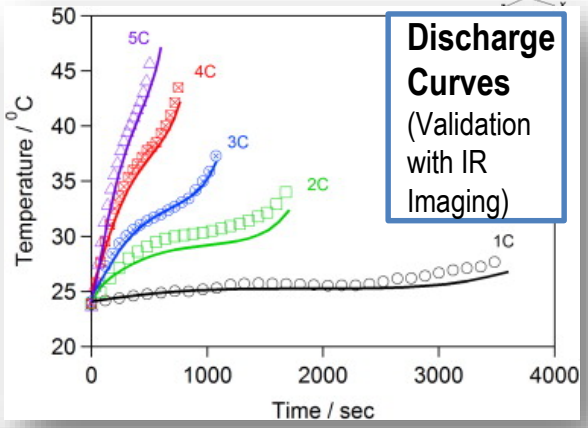
1C Discharge



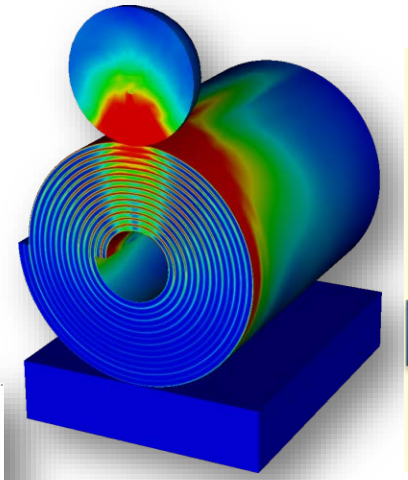
5C Discharge



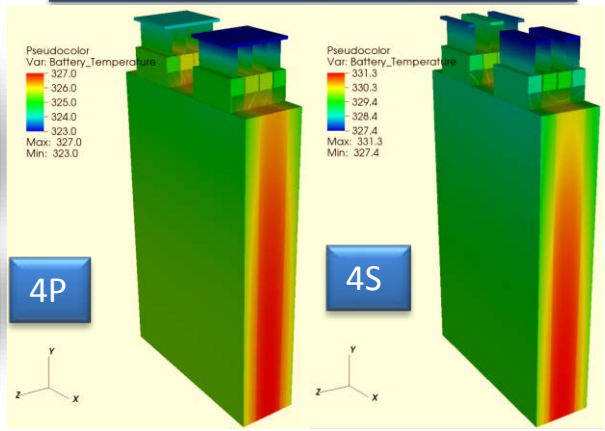
Cylindrical Cell with Current Collectors Resolved (Electrochemical – Thermal - Electrical)



Discharge Curves (Validation with IR Imaging)



Mechanical Abuse of Cylindrical Cell with Current Collectors Resolved (Electrochemical – Thermal – Electrical – Mechanical)



Temperature in 4P and 4S Module with Fully Coupled Electrochemical, Electrical and Thermal Simulations in CAEBAT OAS / VIBE

ELSEVIER

Journal of Power Sources

Available online 24 August 2013

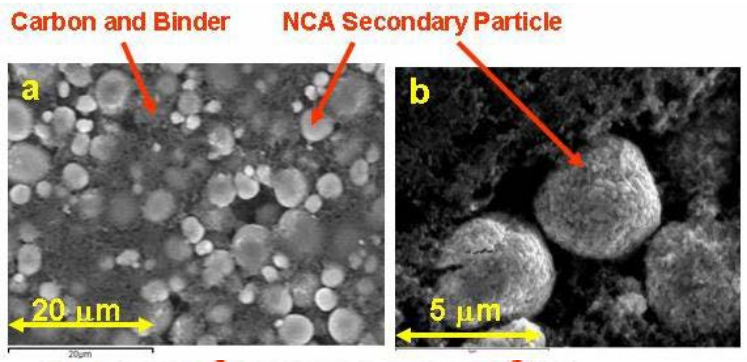
In Press, Accepted Manuscript — Note to users

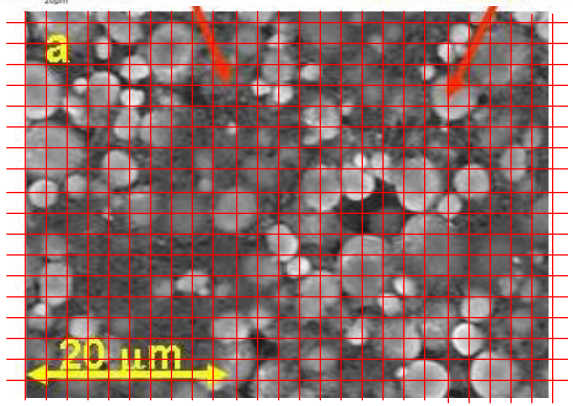
A new open computational framework for highly-resolved coupled 3D multiphysics simulations of Li-Ion Cells ☆

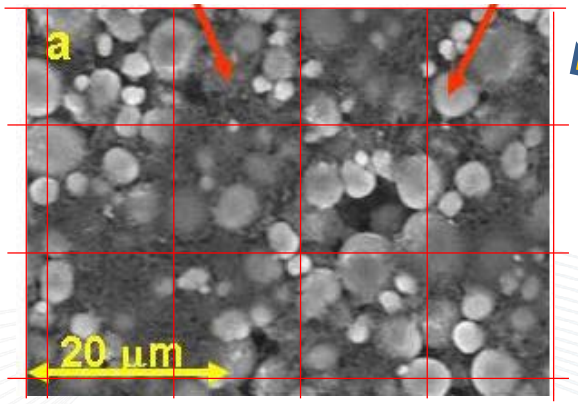
Srikanth Allu, Sergiy Kalnaus, Wael Elwasif, Srdjan Simunovic, John Turner, Sreekanth Pannala

Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN-37831

Electro-chemistry Modeling Hierarchy





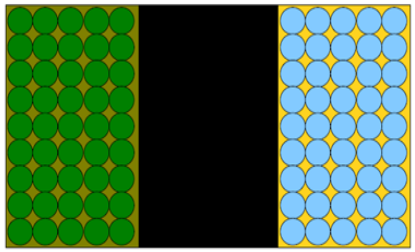


Particle Resolved Formulation

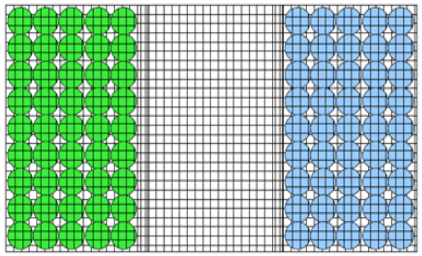
3-D Volume Averaged Formulation

Pseudo-2D

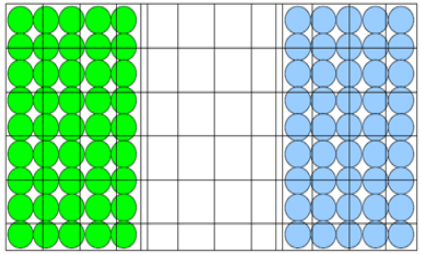
Single Particle



Problem (Typical Lithium-Ion Cell)
(a)



Fully resolved Discretization
(b)



Volume Averaged Representation
(c)

Pseudo-2D
(d)

Single-particle
(e)

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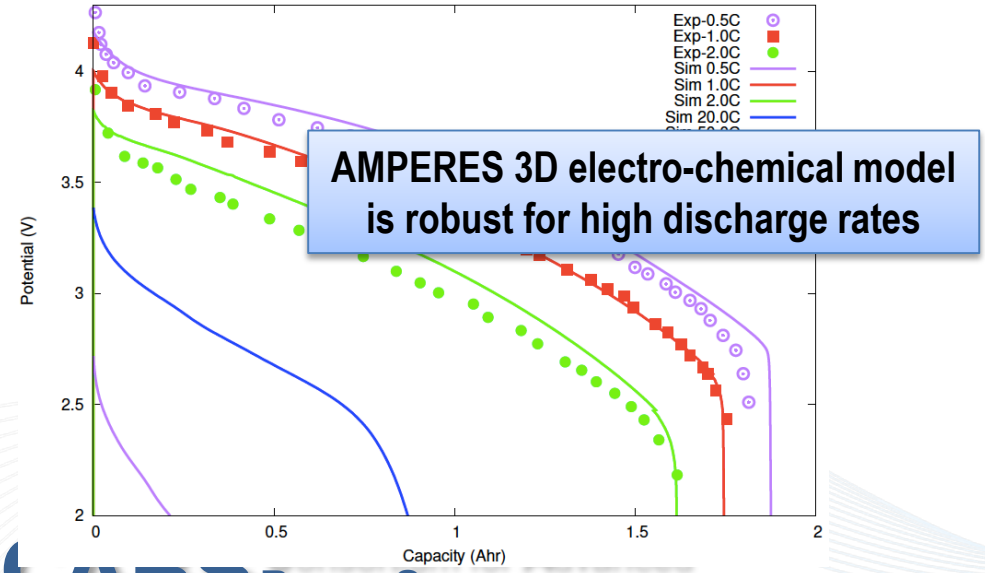
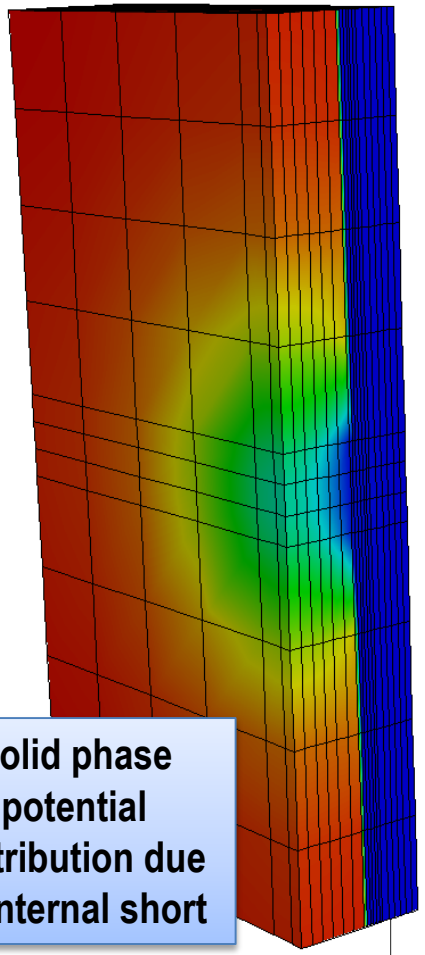
AMPERES is robust enough to handle high discharge rates needed for short simulations

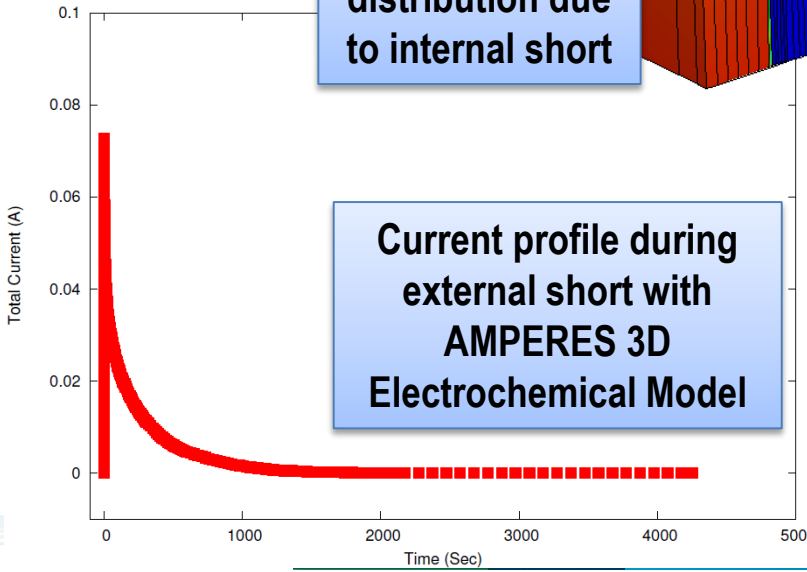
- External short is similar to internal short from an electrochemistry perspective
- Rapidly dropping the potential difference across the terminals in a short time produces exponential rise and decay of current through the battery
  - **Now evolving current as part of simulation rather than imposing**
- Fully 3D – maps directly to electrical / thermal and mechanical
- Runs in a few minutes



AMPERES 3D electro-chemical model is robust for high discharge rates

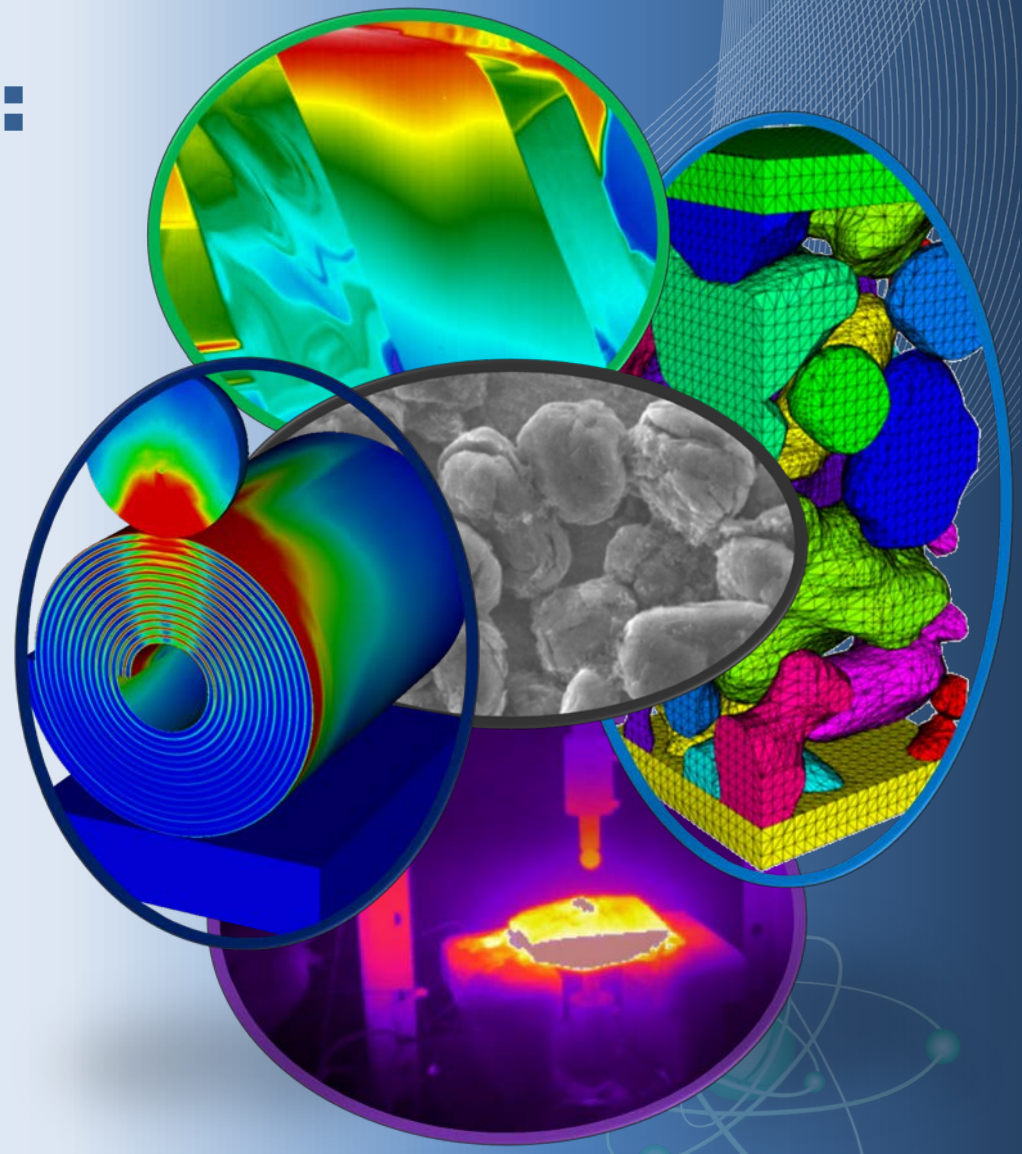


Solid phase potential distribution due to internal short



Current profile during external short with AMPERES 3D Electrochemical Model

Technical Accomplishments:
FY16 Completed Milestones



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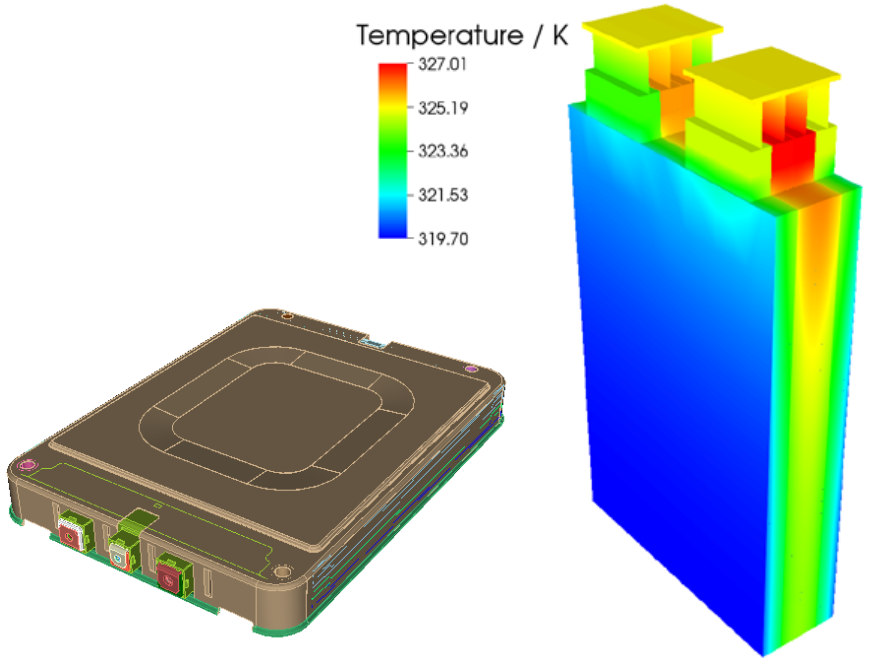
Milestone C.1 - Baseline performance profiling
ORNL Lead, Status: Complete

Goals

- Measure VIBE performance
  - Identify components for improvement / optimization
- Perform simulations involving real automotive battery pack configuration (Nissan Leaf pack is the current choice)
  - Constant current discharge
  - Coupled electrochemical-electrical-thermal simulations under US 06 driving profile



Approach / Strategy

- Select problem
- Generate mesh
- Experimental data for thermal-electrochemical two-way coupling
- Profiling and performance analysis

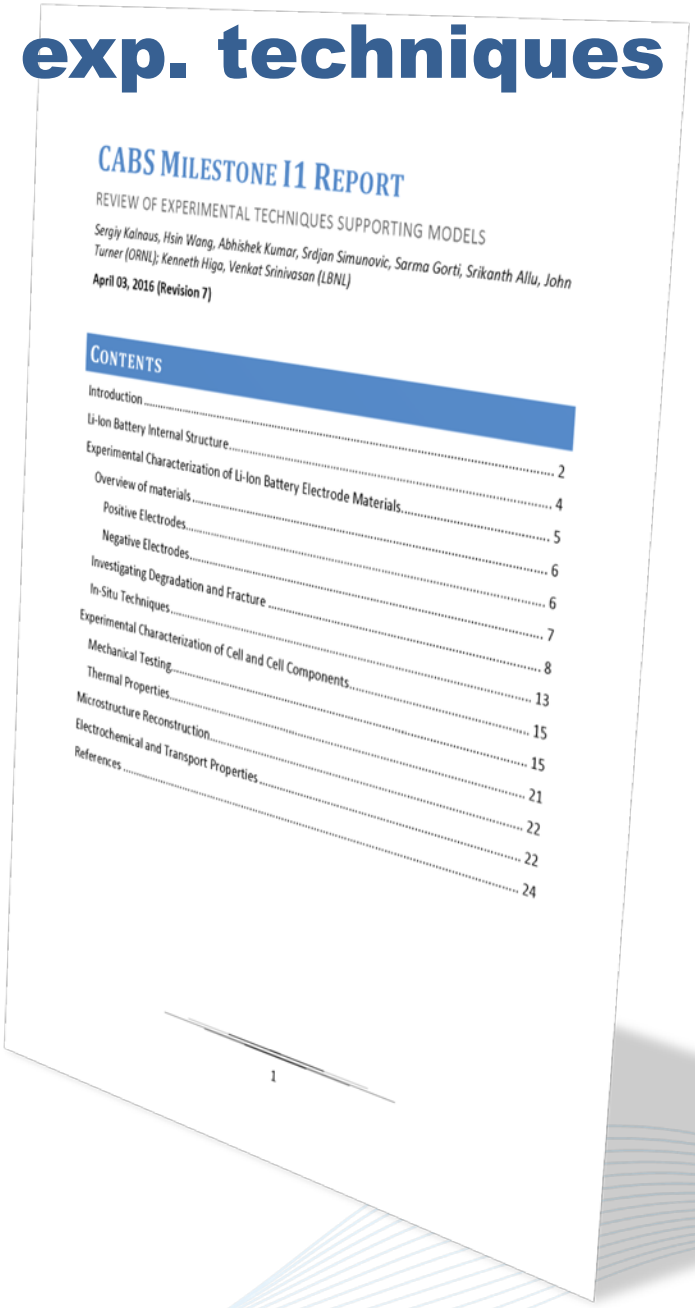
Results

- Constant current discharge of representative 4P module was simulated using NTG and DualFoil models for electrochemistry, nonlinearly coupled to thermal and electrical solutions
- Performance profiling identified opportunity to speed up simulation by 25%

Milestone I.1 - Report on exp. techniques
ORNL Lead
Status: Complete

Goals

- Summarize experimental techniques available to address mechanical and electrochemical behavior of the Li-ion cell and cell components and active materials
  - determination of material properties for model input
  - determination of geometric features of electrodes (microstructure reconstruction) for meshing
  - validation of models
  - benchmark experiments defining failure mode of cells under mechanical abuse



CABS MILESTONE I1 REPORT

REVIEW OF EXPERIMENTAL TECHNIQUES SUPPORTING MODELS

Sergiy Kalnaus, Hsin Wang, Abhishek Kumar, Srdjan Simunovic, Sarma Gorti, Srikanth Allu, John Turner (ORNL); Kenneth Higa, Venkat Srinivasan (LBNL)

April 03, 2016 (Revision 7)

CONTENTS

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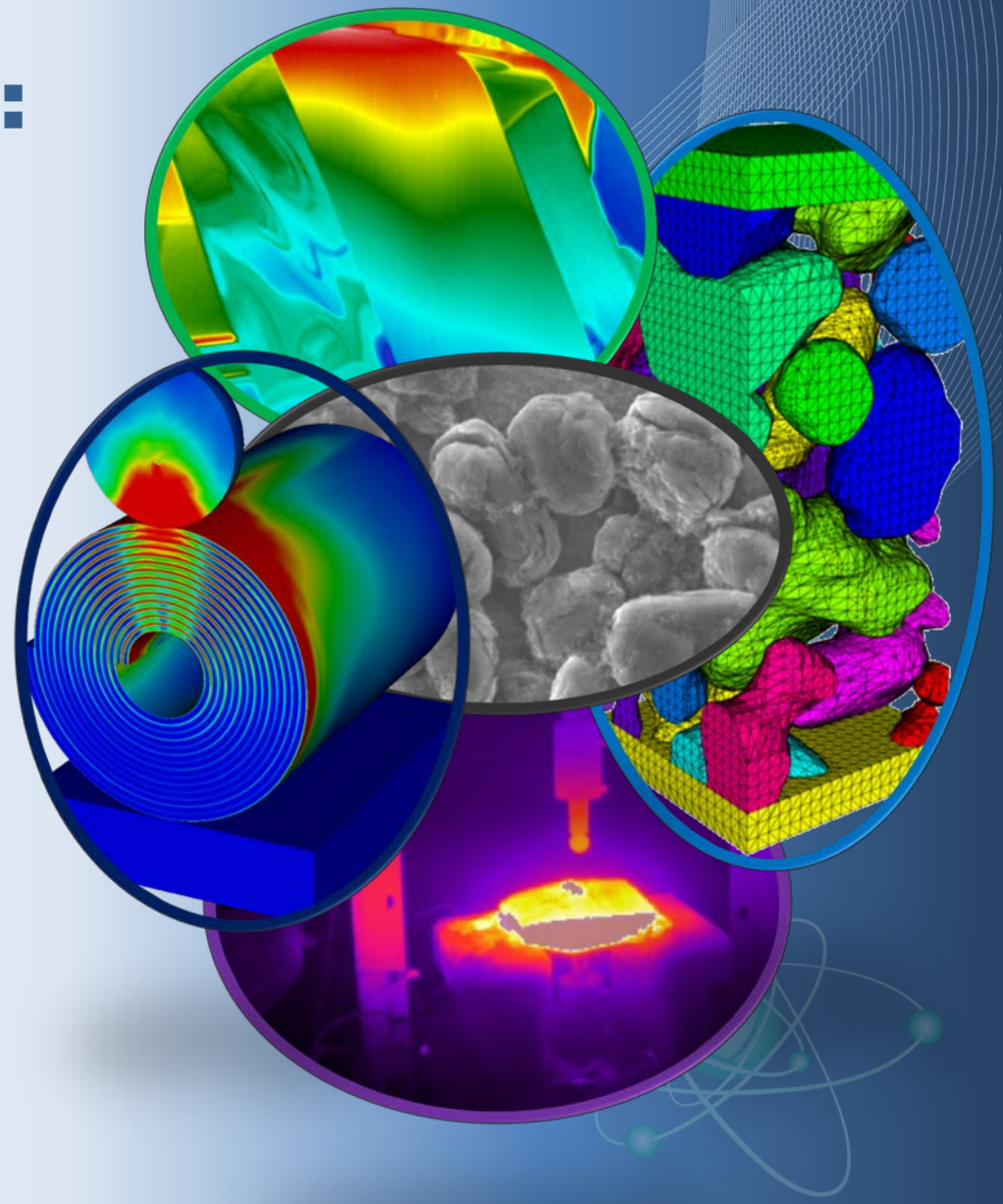
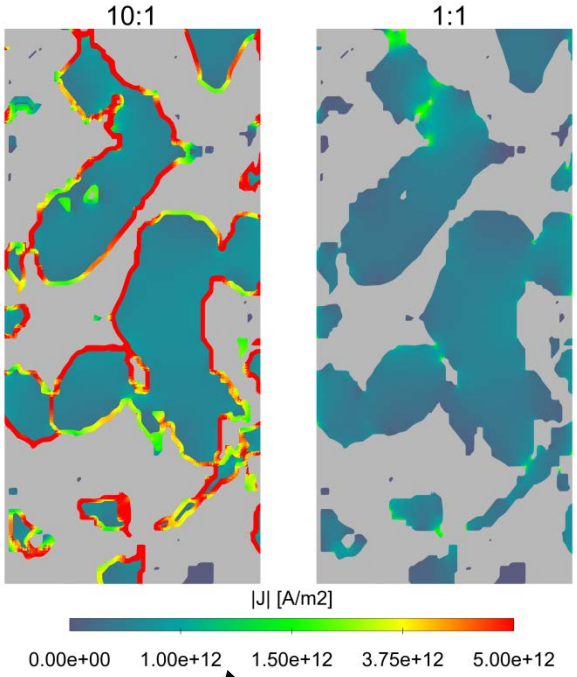
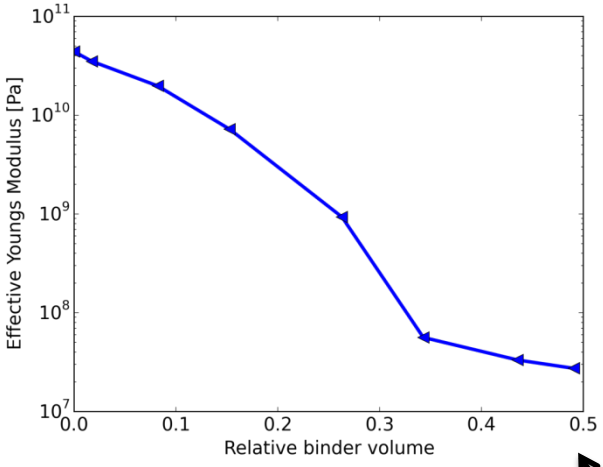
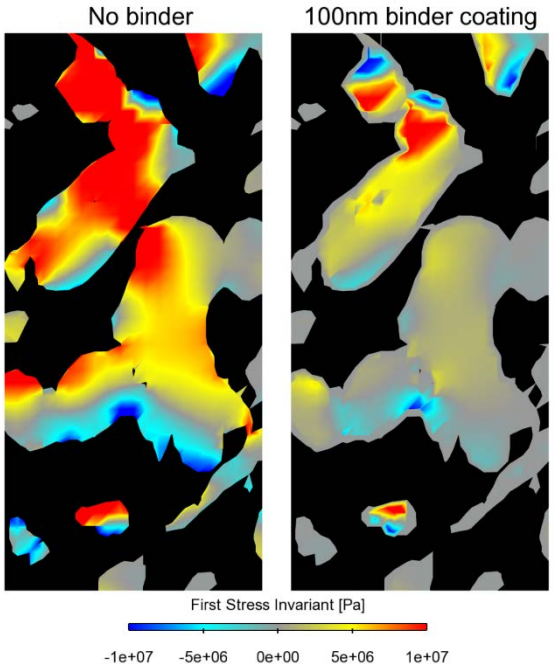
Technical Accomplishments:
Other FY16 Accomplishments



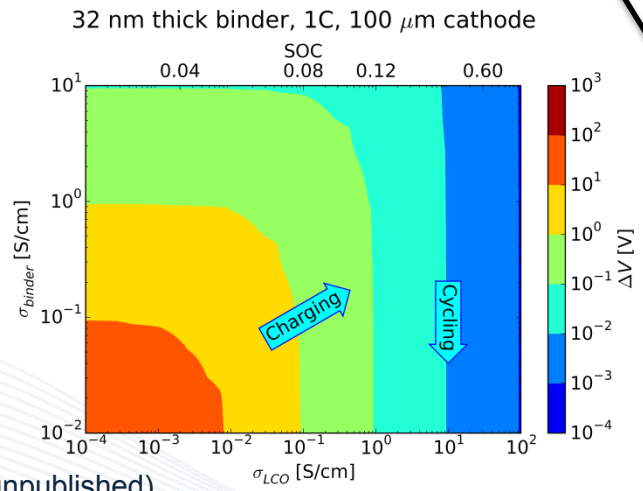
Effective properties with binder







Effective conductivity: Stress/cycling degrades binder conductivity, reduces accessibility of some LCO concentrations

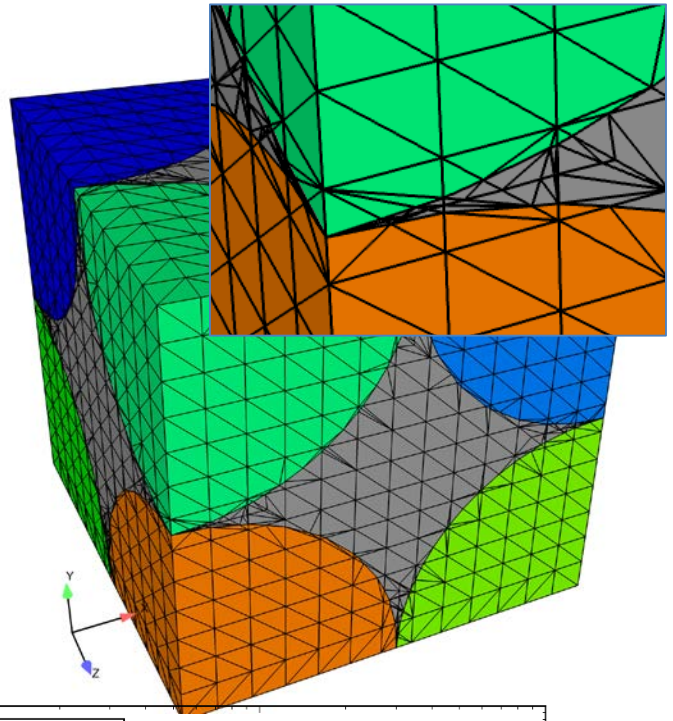


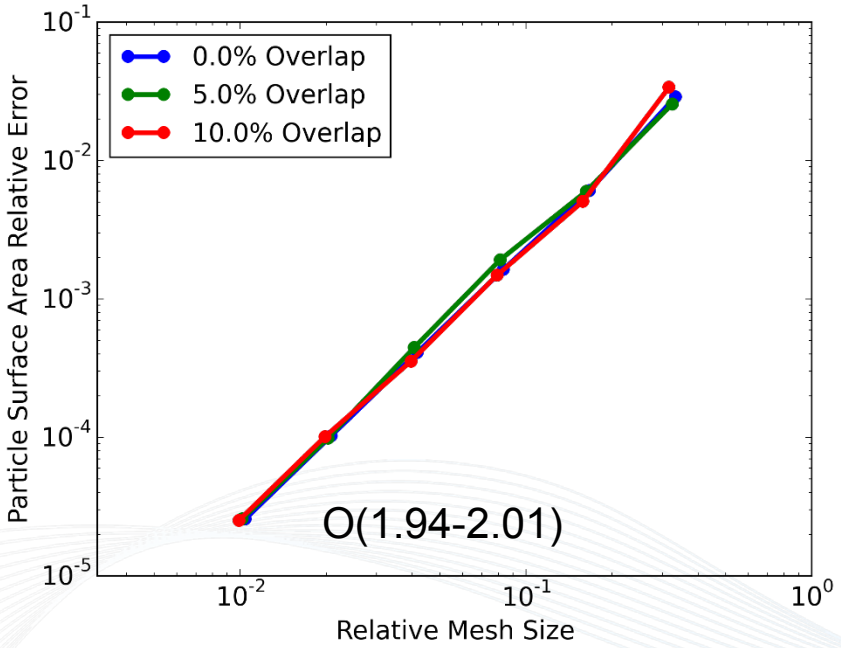
Effective modulus: Soft binder significantly decreases stress state throughout network

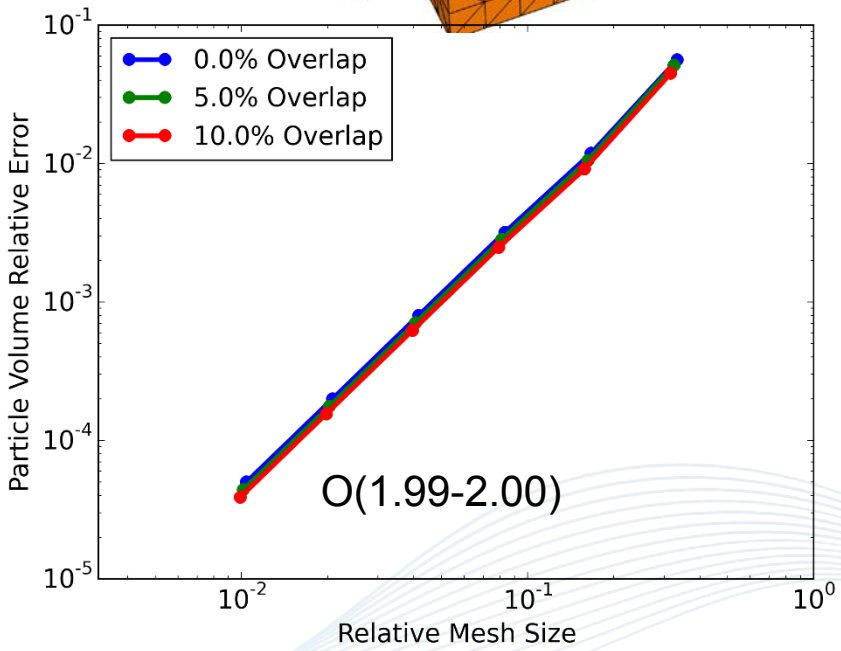
Mendoza, Roberts, et al. (submitted); Roberts (unpublished)

Separate cP spheres: Geometric convergence

- Geometric parameters now show clear 2nd-order convergence w/ low initial error
- < 1% error in SA and volume at $h \approx r/5$!
  - With single LS, required $h \approx r/100$.

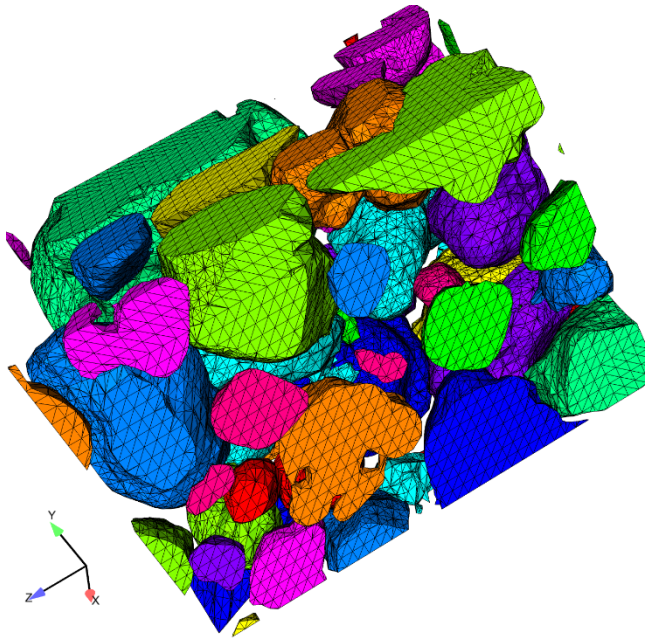


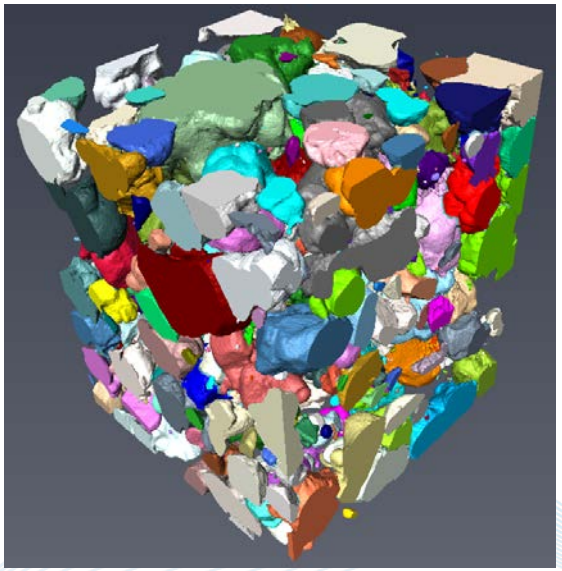




Performance scaling: Many particles

- Currently performing verification activities on 200 particle mesh; largest currently feasible
- Goal of simulating domain with 700 particles
- Recent improvements for particle-number scaling
  - Former behavior $< n^3$
  - Recent improvements $> n$





Particles	4.39.5	STK Part Creation	Crossings Map	Volume-Surface Map
100	1.68	1.70	0.77	0.40
200	12.25	9.00	4.17	1.00
Scaling	7.3x	5.3x	5.4x	2.5x

FY17 preparation: PFG-NMR and concentrated solution theory

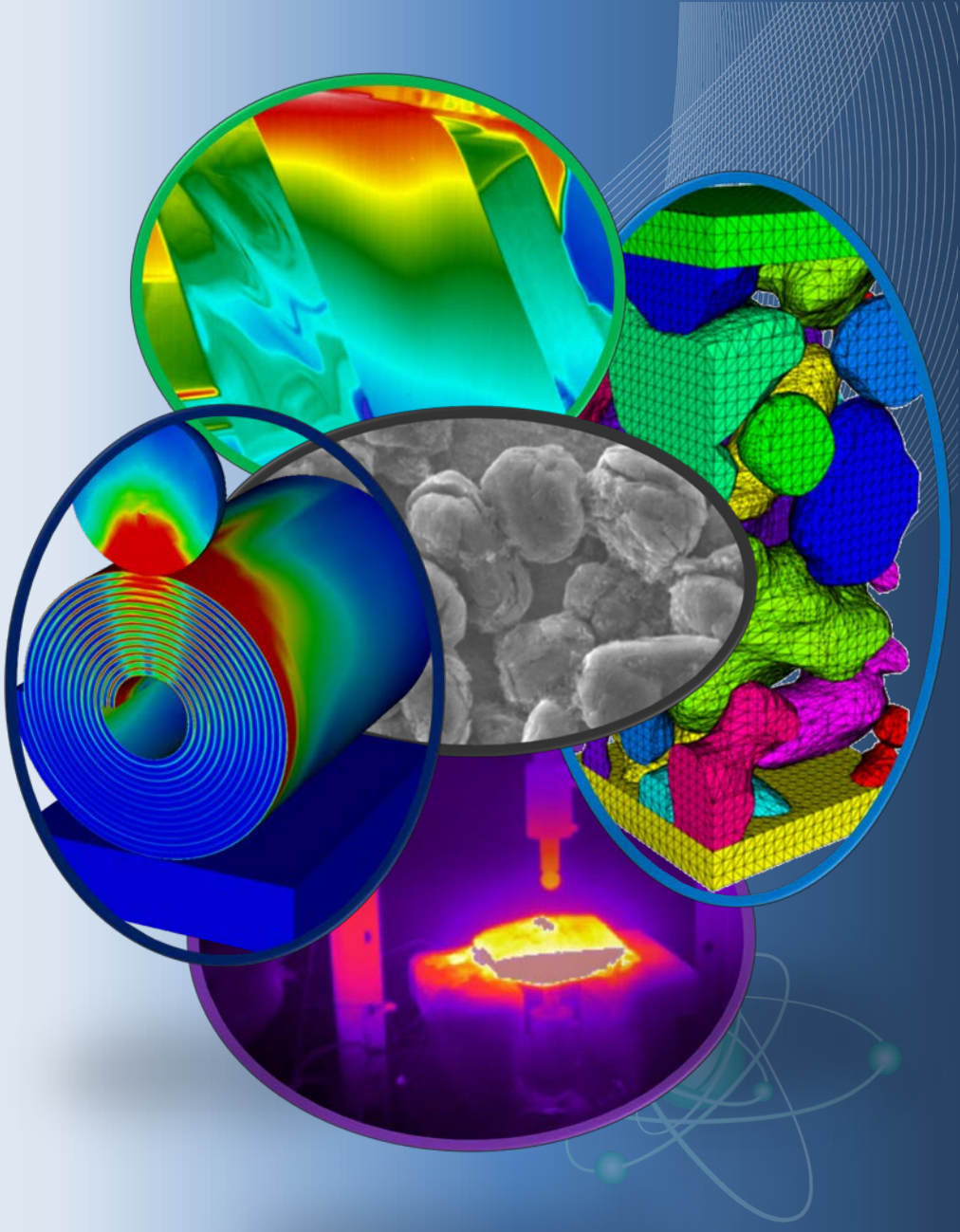
- High electrolyte concentrations develop in batteries under demanding conditions
- At high concentrations, all species in solution interact with all others; Fick's law no longer appropriate, accurate models require concentrated solution theory
- Pulsed field gradient (PFG)-NMR yields tracer diffusivities
- Have developed method for connecting PFG-NMR measurements to concentrated solution theory multicomponent diffusivities

$$\begin{pmatrix} j_1/\rho_1 \\ j_2/\rho_2 \\ j_3/\rho_3 \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} & L_{13} \\ L_{12} & L_{22} & L_{23} \\ L_{13} & L_{23} & L_{33} \end{pmatrix} \begin{pmatrix} d_1 \\ d_2 \\ d_3 \end{pmatrix}$$

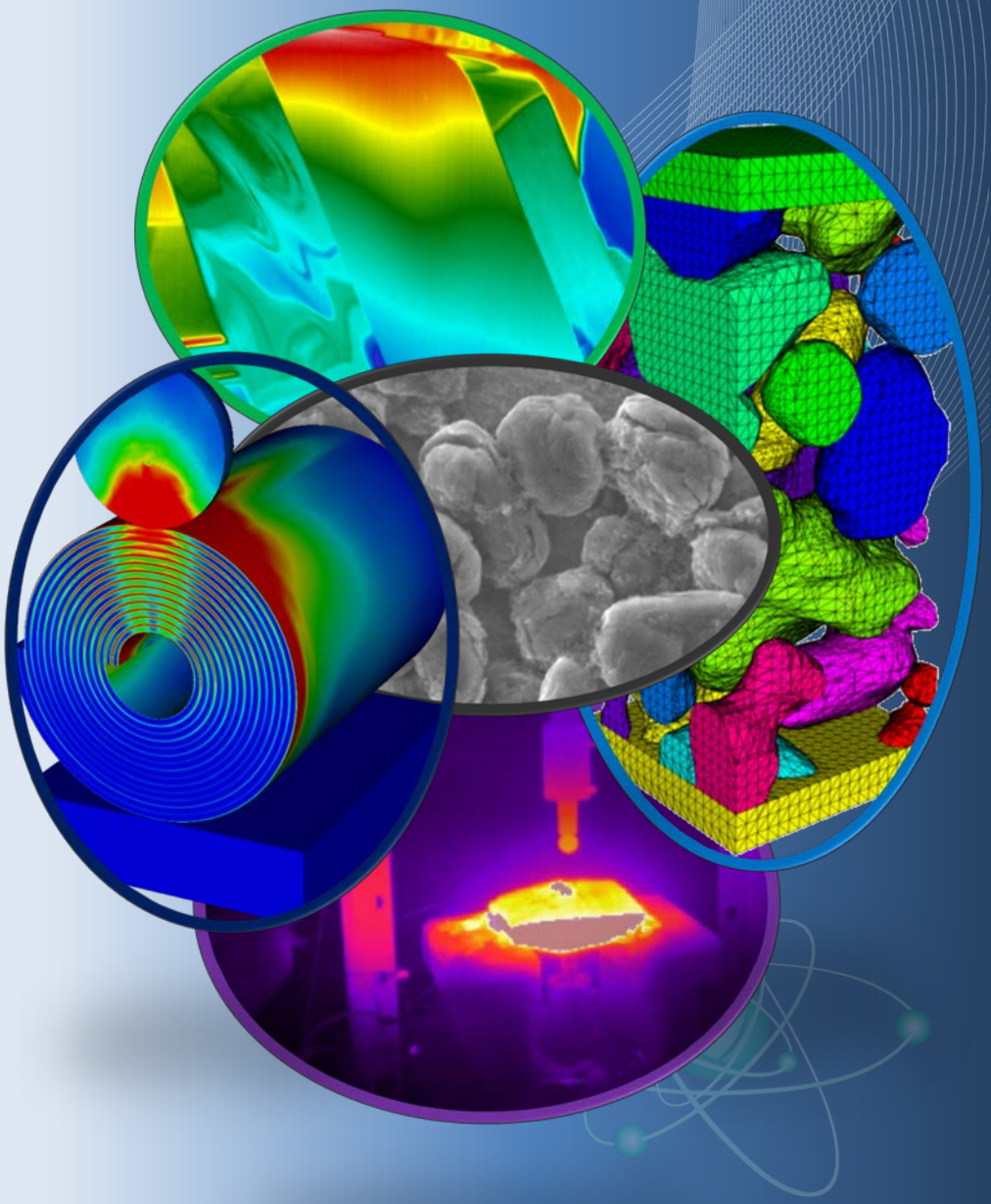
$$d_k = x_k \left(1 + \frac{d\ln\gamma_k}{d\ln x_k}\right) \nabla x_k$$

Response to Previous Year Reviewers' Comments

This is a new project for FY16



Collaboration and Coordination



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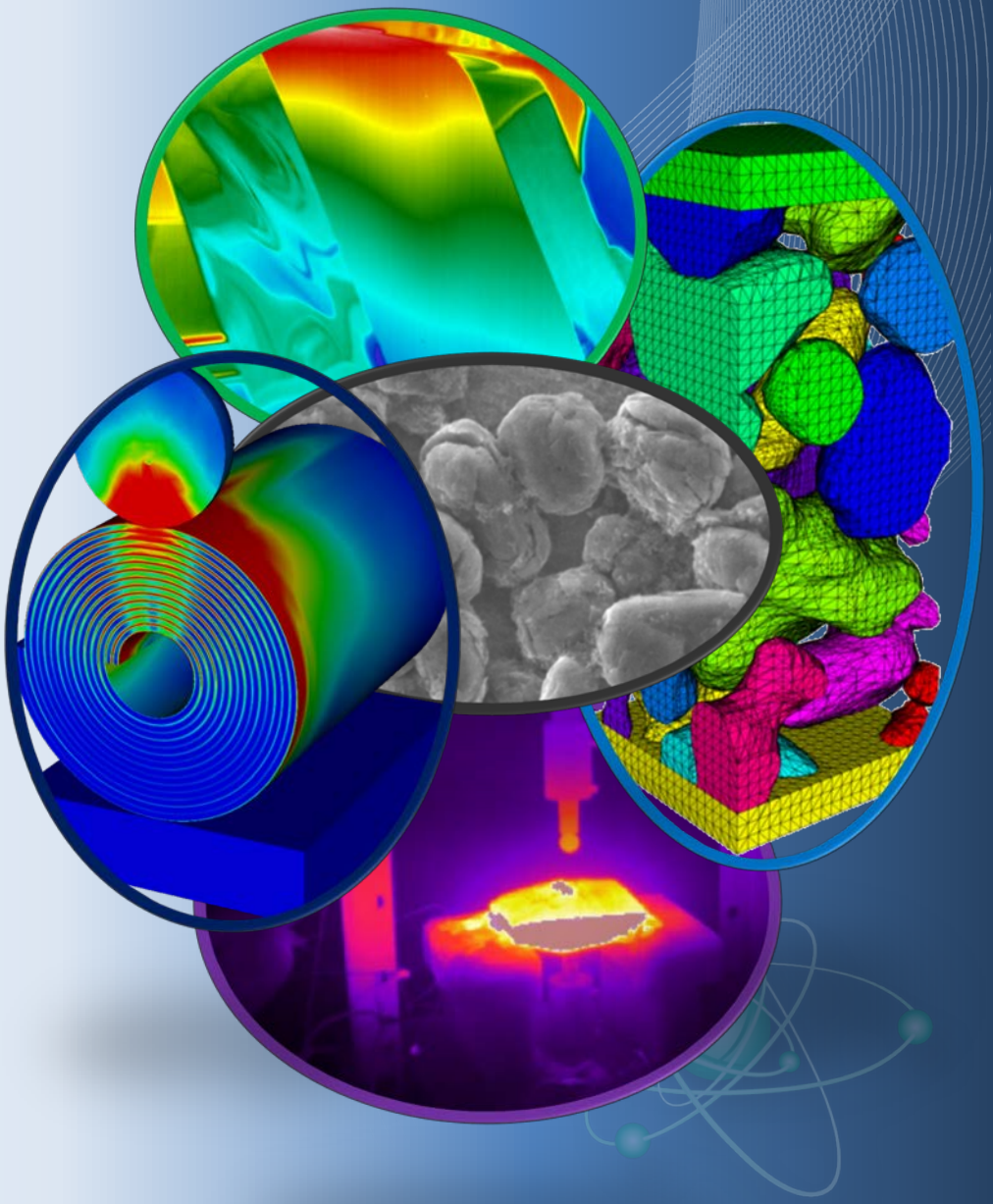
Collaboration and Coordination

- Bi-weekly telecons of working groups on meshing and testing between CABS and NREL project team.
- Monthly videocons with CABS partners at SNL and LBNL
- Joint quarterly meetings with VTO program office and NREL project team
- Partner with Ford on VTO-funded project on simulation of mechanical abuse (Project ID: ES296)
- Project with DOT / NHTSA on crashworthiness
- Naval Surface Warfare Center, Carderock for large-scale testing
- Interactions with VIBE users and potential users, e.g.
  - Motorola
  - NASA

Remaining Challenges and Barriers



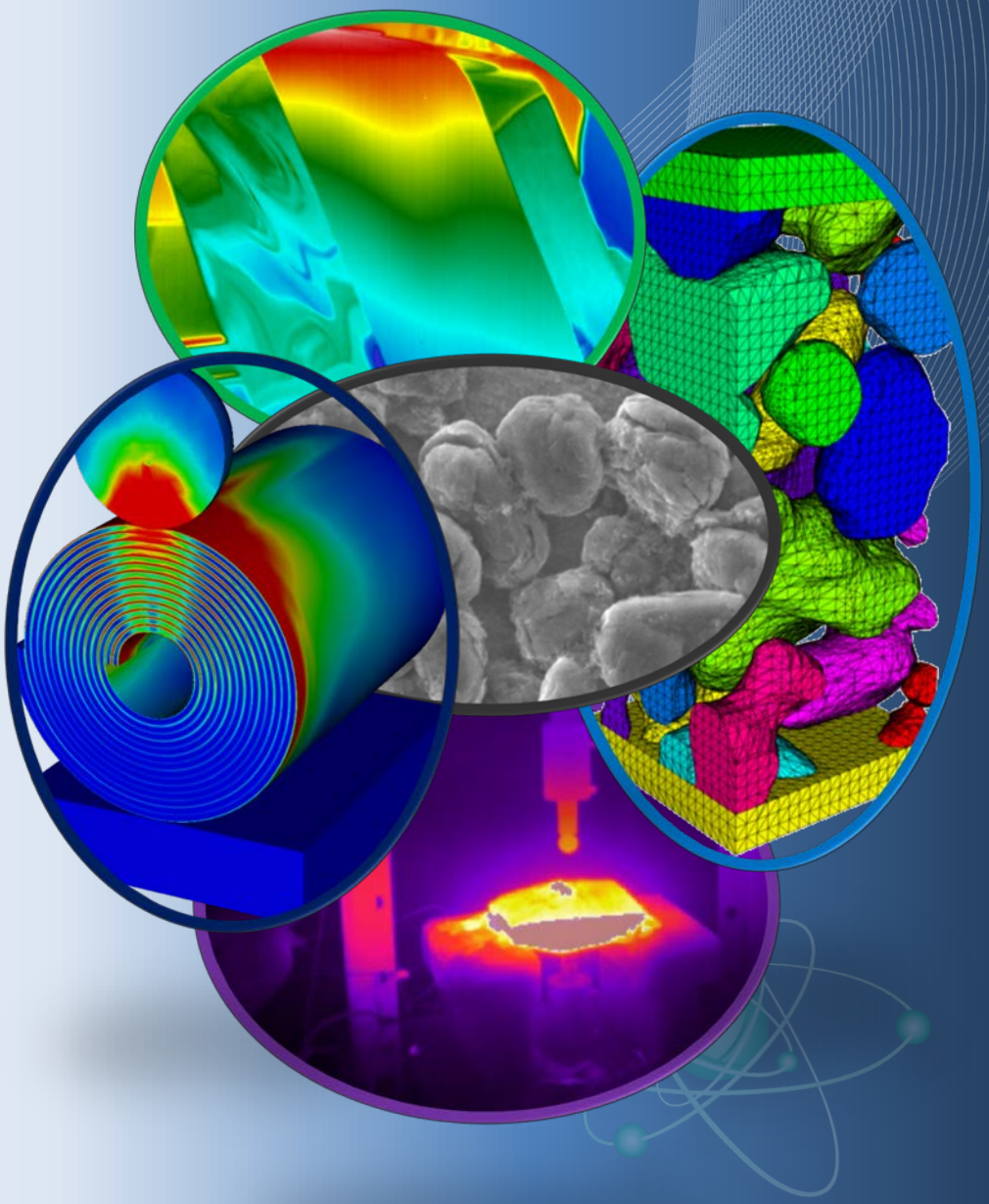
Upcoming challenges

- Software and numerical challenges of
  - scaling to larger problems (pack level, with multiple domains)
  - scaling microstructure simulations
  - multiscale simulations (embedding subgrid models in continuum simulations)
- FY17, Q2: Quantifying the error in transport properties due to ion pairing.
- FY18, Q1: Constructing appropriate sample holders for X-ray tomography of cycled electrodes.

Future Work

Includes:

- Detail on FY16 milestones
- Overview of FY17 and FY18 milestones



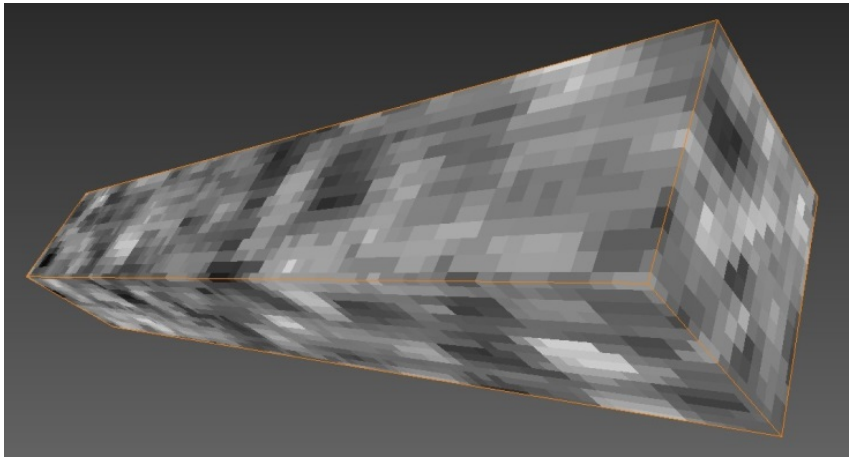
Milestone E.1 - Microstructure imaging
LBNL Lead, Status: On Track

Goal

- Obtaining tomography images from uncycled electrodes.
- Perform microstructure imaging of electrodes calendered to different pressures

Approach / Strategy

- X-ray microtomography of electrode samples under light compression, immersed in electrolyte solution
- Refine methods for associating voxel intensity with phase identity
- Generate segmented reconstructions of NMC electrodes, uncalendered and calendered, at 3 pressures



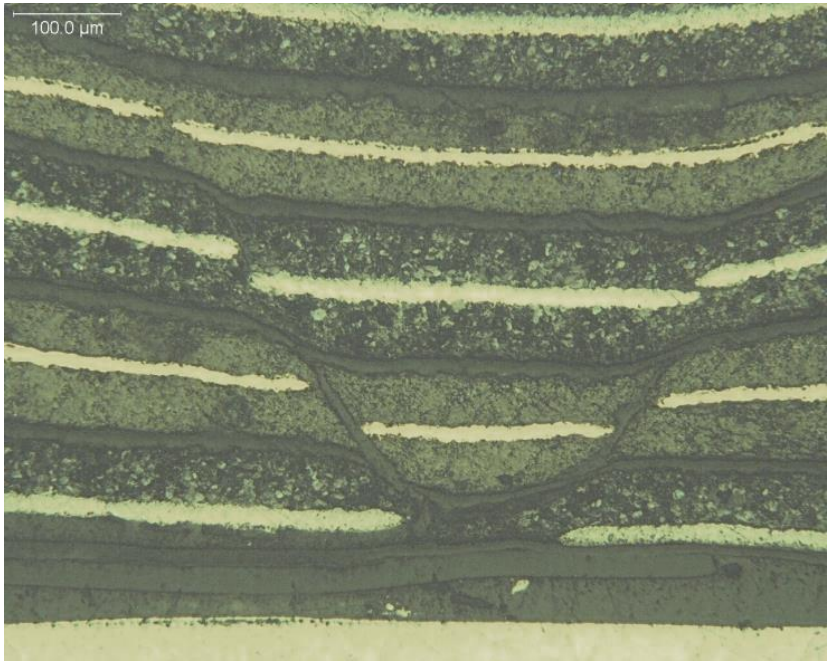
Challenges

- Ability to determine phase identity
- Mitigation – use alternative measurements (BET, etc.) to supplement reconstruction data

Milestone E.2 - Single side incremental indentation
ORNL Lead, Status: On Track

Goals

- Explore internal deformation of the cell including internal faulting
- Provide experimental support for formulation of cell failure criterion



Approach / Strategy

- Design enclosure to preserve internal state of the cell after removal of load.
- Investigate effect of indentation speed on onset of short circuit

Challenges

- Safety concerns for high SOC scenarios may result in using backup test facility (NSWC)

CABS FY17 Milestones

IDs indicate whether milestones are primarily experimental (E), computational (C), or integrated (I).

ID	FY17	Lead	Q1	Q2	Q3	Q4	Risk(s)	Mitigation
I.3	Demonstration of ability to construct 3D meshes of electrodes using reconstructions from micro-tomography	SNL	P				Availability of data, ability to create meshes	Use existing data and meshes
E.3	Potential-dependent solid diffusivities for Li-ion and EIS	LBNL		P			Ability to obtain nucleation rate, location	Use average quantities
I.4	Demonstrated ability of VIBE/OAS to simulate onset of short-circuit due to mechanical abuse informed by microstructure	ORNL		D			Ability to handle mesh distortions	Use alternative element formulation
E.4	Data from mechanical deformation tests (nano-indentation and scratch tests) available	ORNL			P		Ability to procure and configure test equipment	Adjust schedule
C.2	Validated constitutive models and failure criteria for electrode materials and spirally wound, wound prismatic, and stacked electrodes under indentation	ORNL				P	Convergence of constitutive models	Explore alternative solution algorithms
I.5	Deployment of VIBE/OAS with integrated multiscale capability	ORNL				S	Ability to simulate sufficiently large domains	Obtain additional comp. resources

CABS FY18 Milestones

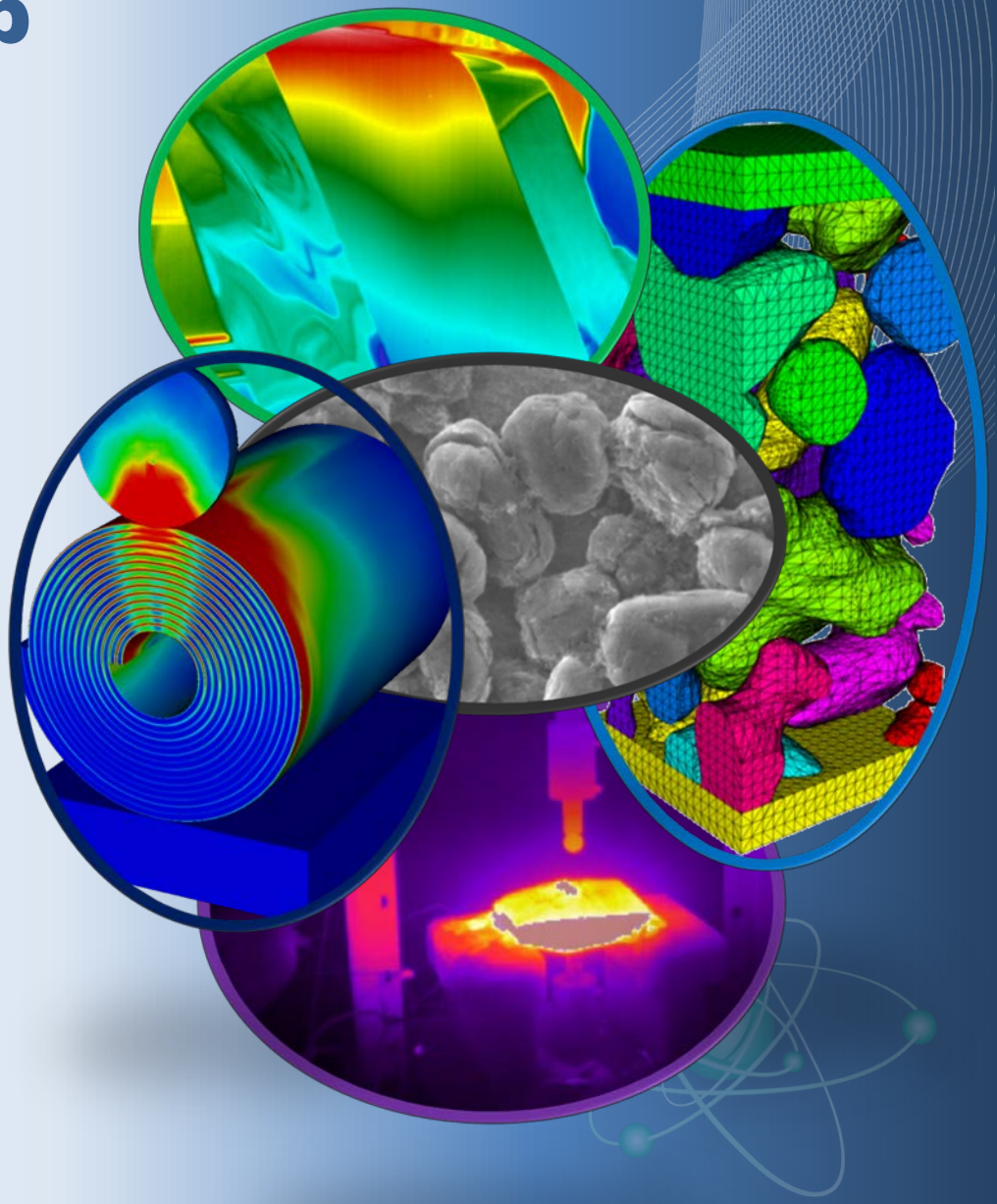
IDs indicate whether milestones are primarily experimental (E), computational (C), or integrated (I).

ID	FY18	Lead	Q1	Q2	Q3	Q4	Risk(s)	Mitigation
C.3	Coupled thermo-electro-mechanical microstructure simulations of overcharge and mechanical abuse scenarios	SNL	P				Ability to accurately handle large deformation and fracture	Accept more approximate models
E.5	Obtain electrode image data from cycled electrode material	LBNL	P				Ability to cycle consistently	Increase samples
C.4	Demonstrated mesoscale simulations	ORNL		P			Input param. uncertainty	Careful design of exp. param. space
C.5	Demonstrate improved computational efficiency on benchmark pack-level sim using hierarchy of electrochemical models for US06 drive cycle	ORNL			P		Unforeseen software and numerical challenges	Adjust priorities and reallocate staff
C.6	Demonstration of validated constitutive models & failure criteria for electrode materials & spirally wound, wound prismatic, & stacked electrodes under bending for pouch cell	ORNL				P	Convergence of constitutive models	Explore alternative solution algorithms
I.6	Deployment of VIBE/OAS with efficient, validated mechanistic models	ORNL				S	Availability of data, software challenges	Reallocate staff, approx. data & models

Summary

- We are developing an improved battery simulation tools building upon previously released OAS/VIBE
  - We have done baseline performance profiling of VIBE/OAS/AMPERES and identified strategies for improvement
    - e.g. 25% speedup by eliminating driver setup at each time-step
- We are developing experimental procedures for support of constitutive models and validation. Experimental work is on track
  - Mechanical compression of cells and cell components
  - Resonant ultrasound spectroscopy (RUS)
  - Calendering of electrodes
  - Electrodes for X-Ray tomography prepared and shipped to LBNL
  - Design single side indentation experiments and tensile testing
  - Design experiments for measuring diffusivities in concentrated solutions
- Microstructure simulation capabilities are developed
  - Simulations show significant role of binder in relieving stress inside particles of active electrode material
  - Improved treatment of conformal decomposition FEM (CDFEM) for better convergence

Technical Back-Up Slides



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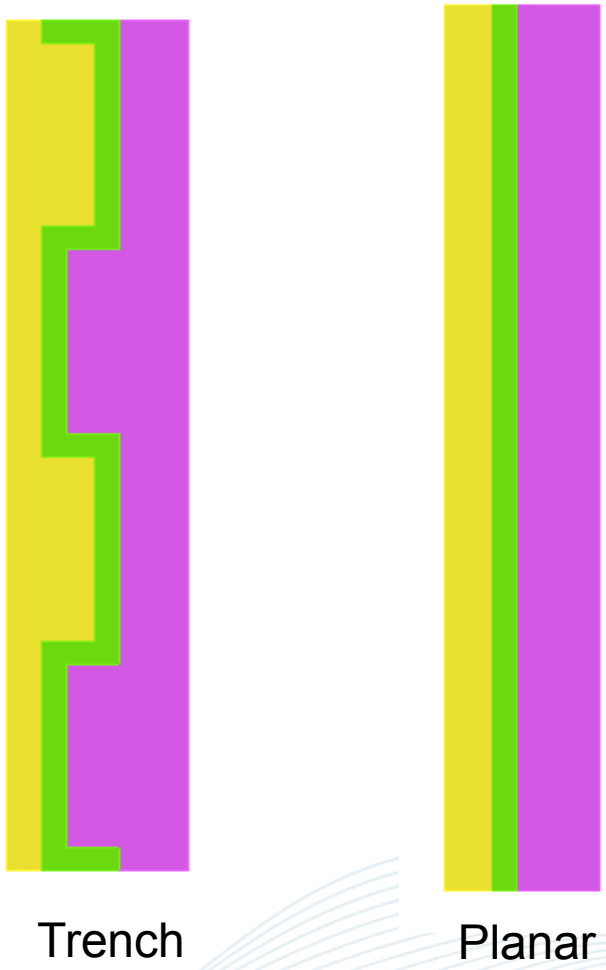
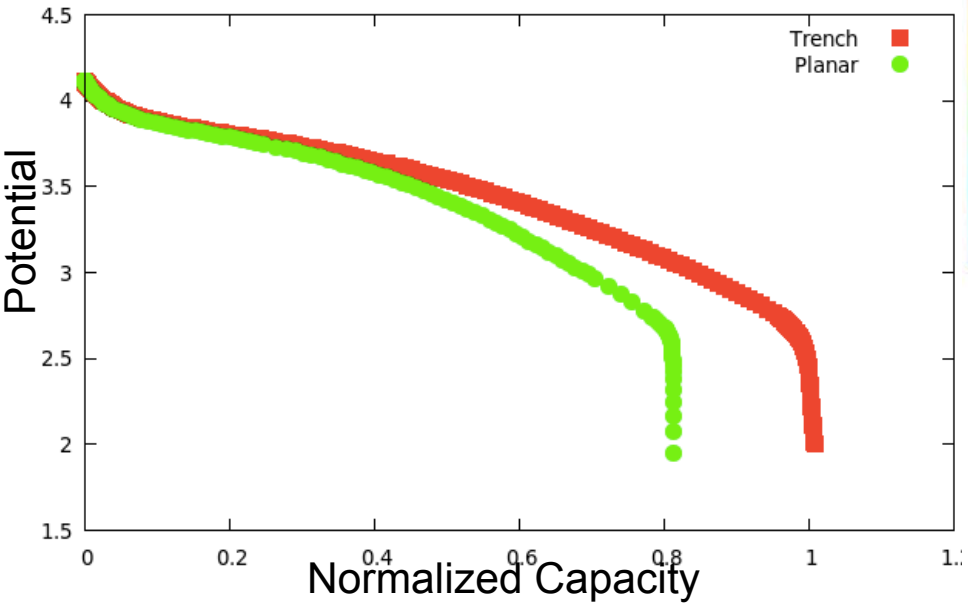
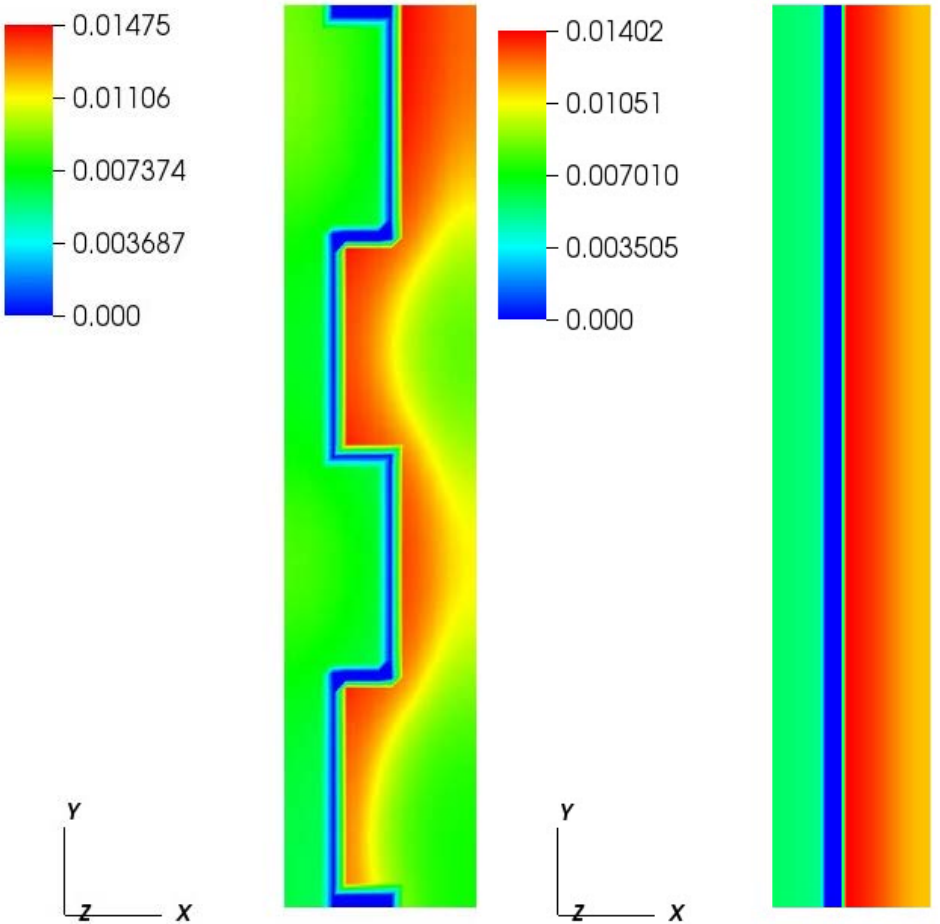
Initial investigation of 3D architecture as a mechanism for increasing energy and power density

- Constant electrode volume for both trench and planar configurations
- To use uniform separator thickness need to maintain equal depth trenches for both electrodes
- Same constant current boundary condition used in both configurations



Comparison between Trench and Planar configurations for 2C discharge

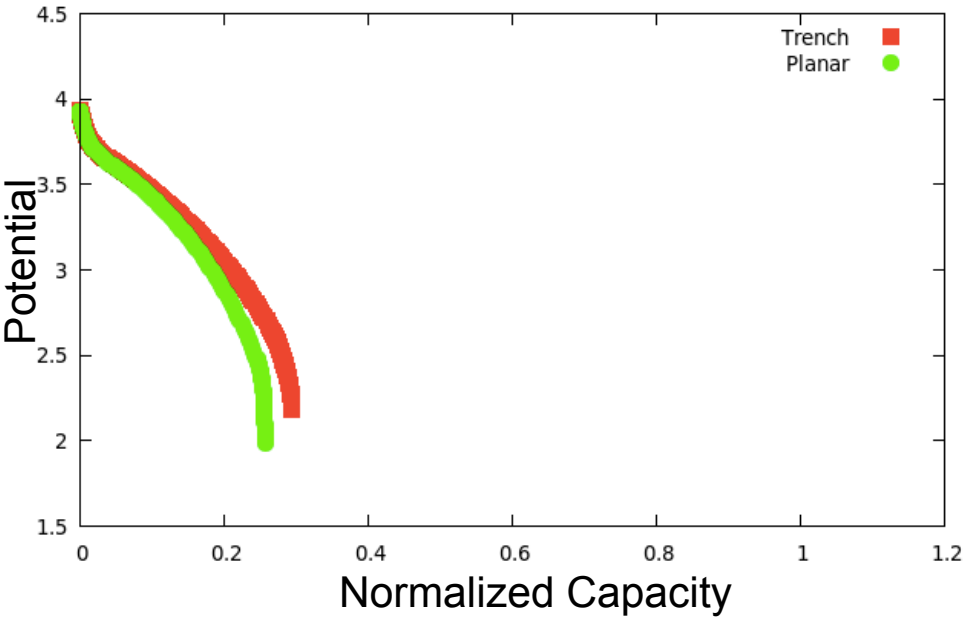


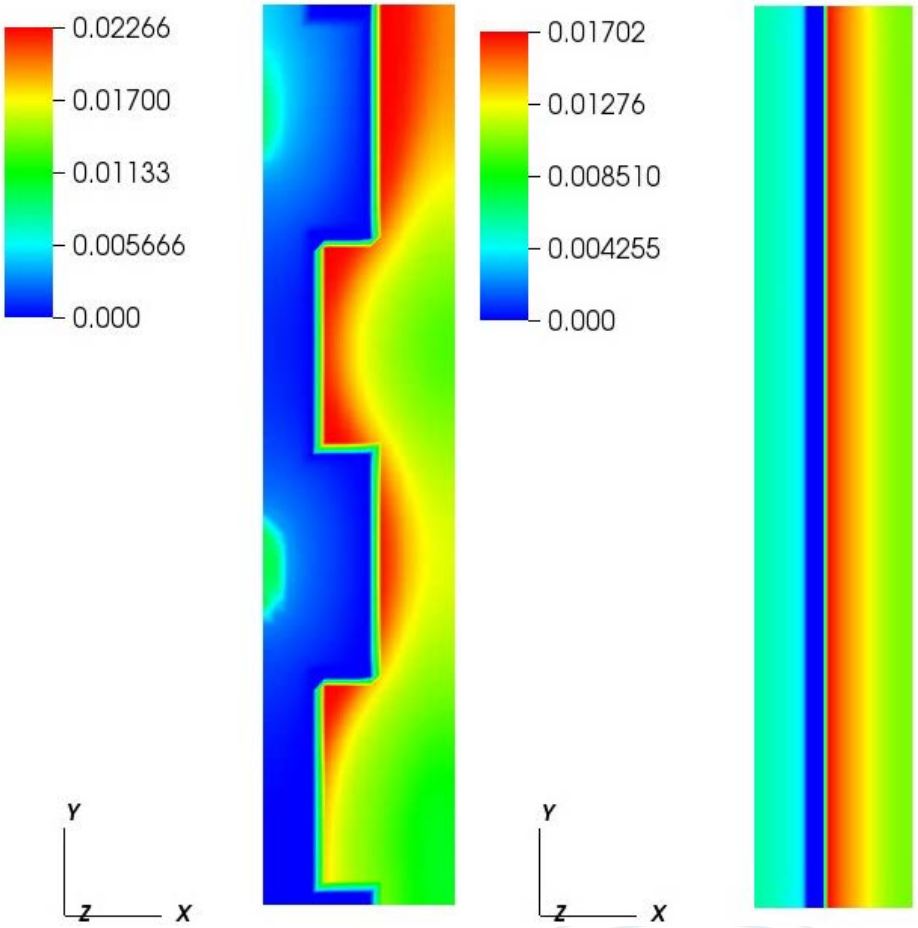


Li Concentration
Solid Phase

Total capacity extracted from trench configuration exceeded the planar configuration at 2C constant current.

Comparison between Trench and Planar configurations for 5C discharge

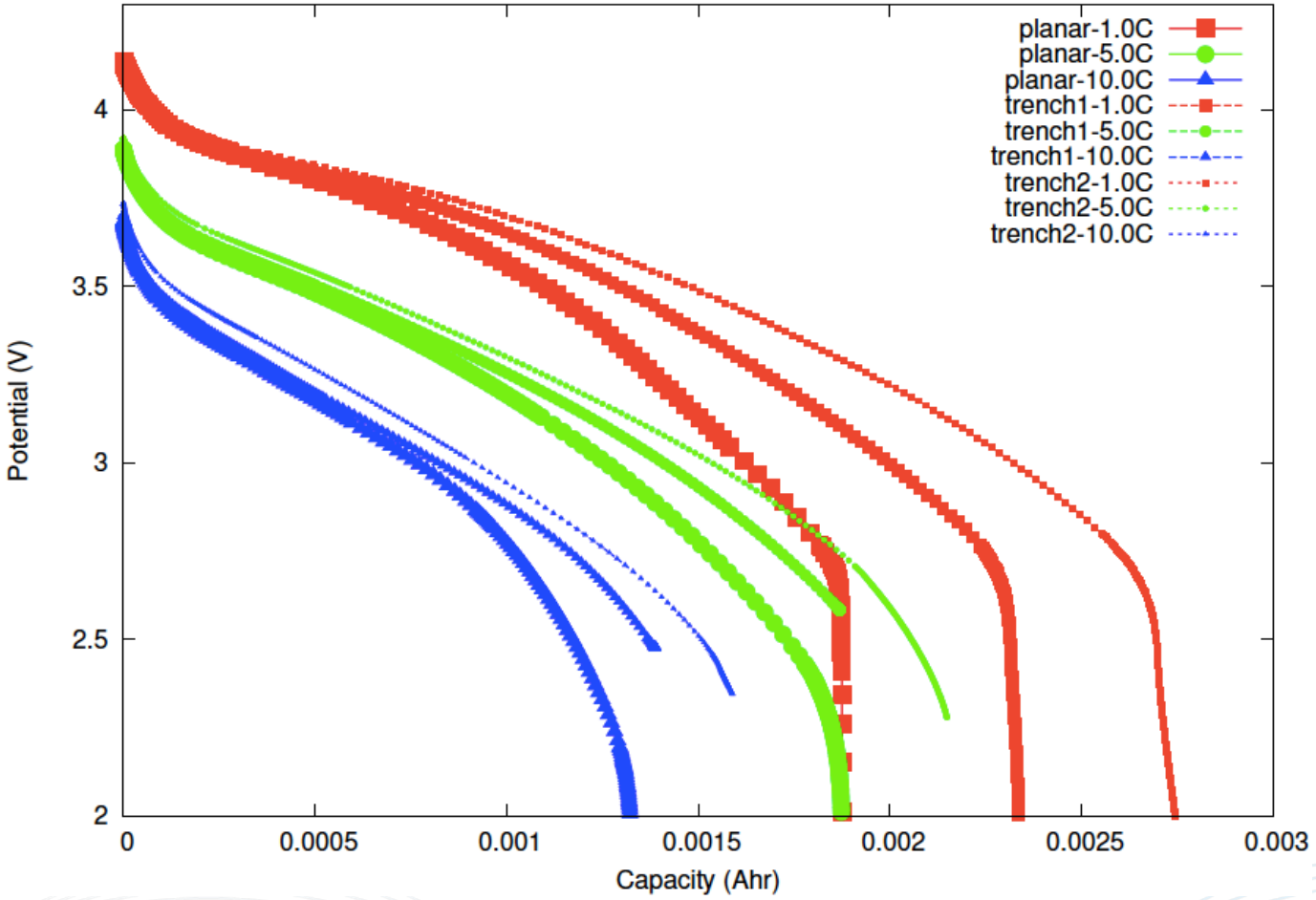




Li Concentration
Solid Phase

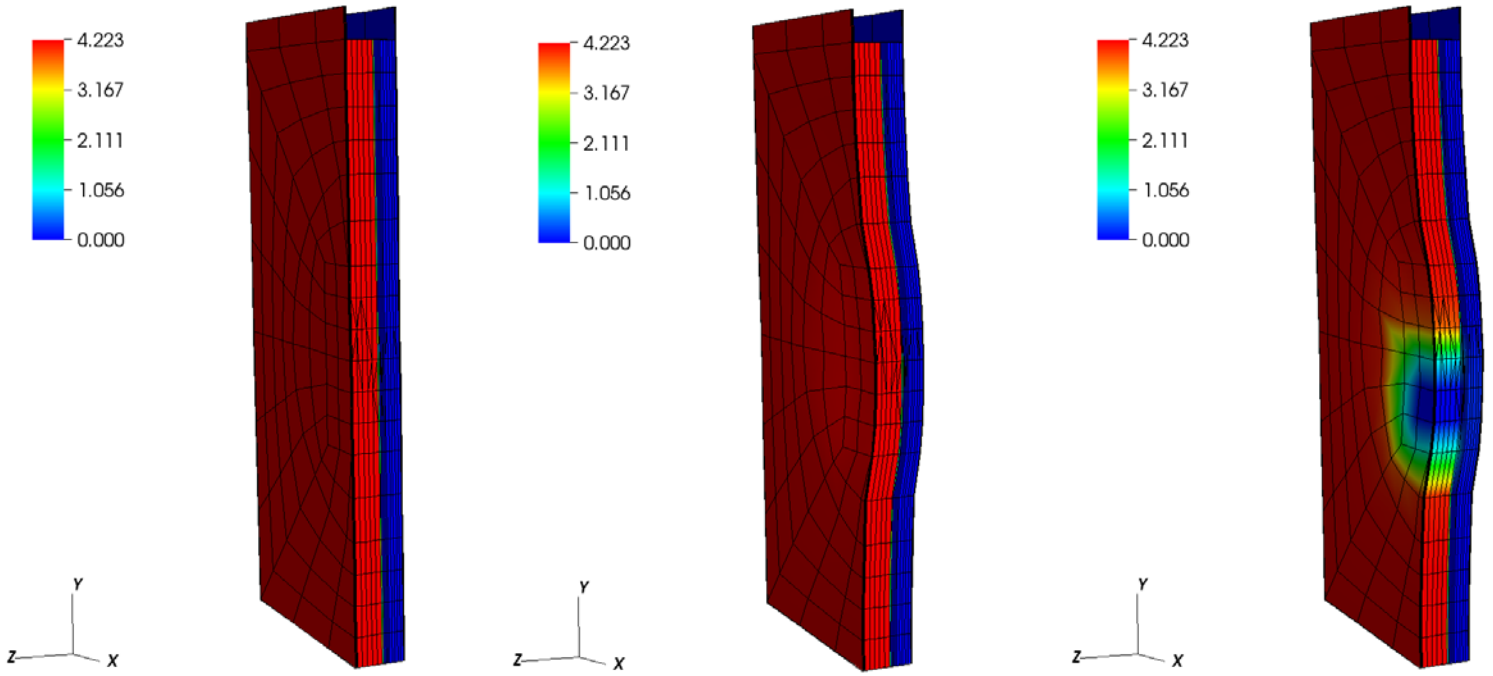
Total capacity extracted from trench configuration exceeded the planar configuration at 5C constant current.

Comparison between Trench and Planar configurations for 1C, 5C, and 10C discharge



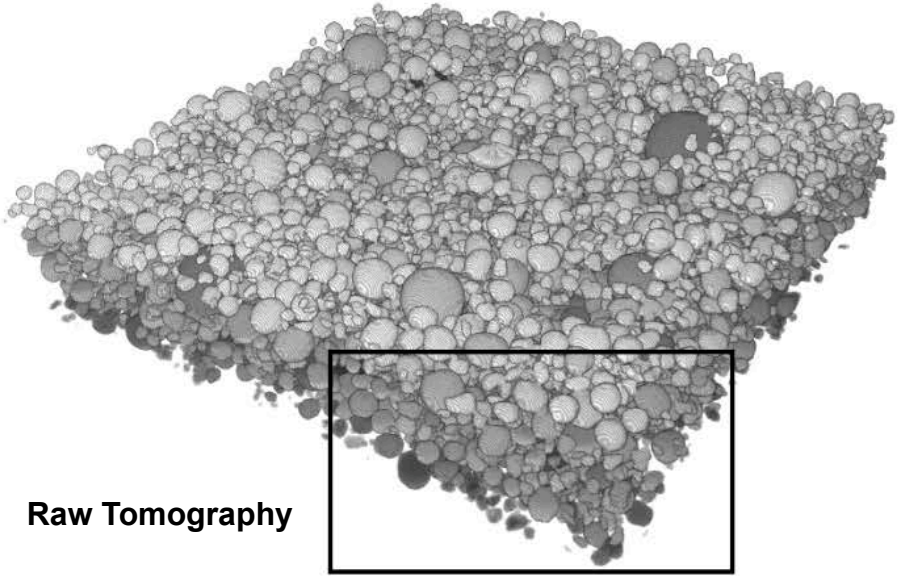
Total capacity extracted from trench configuration exceeded the planar configuration

Integration of resistivity models

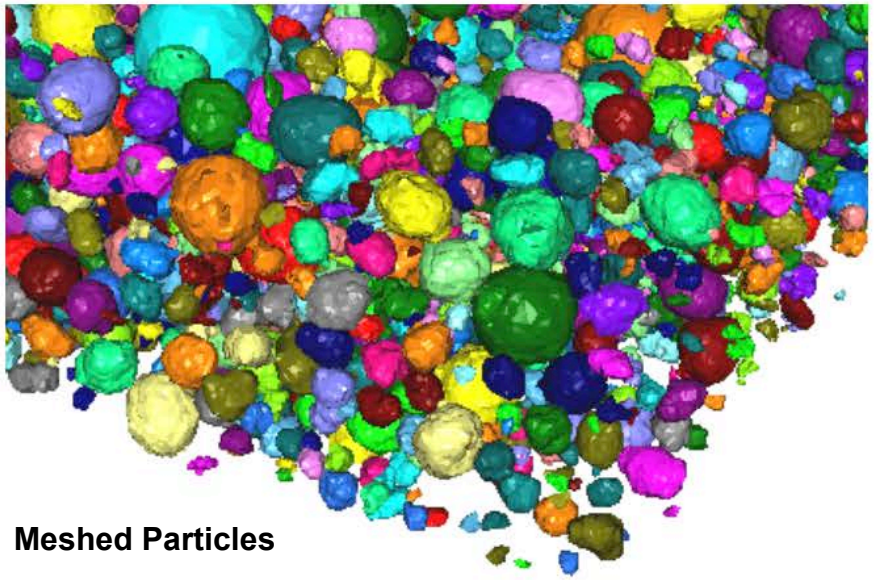


- Integrating the mechanics simulations with resistivity models that feeds into the electrochemistry-thermal simulations.
- Images show potential distribution during internal short with increasing conductance.

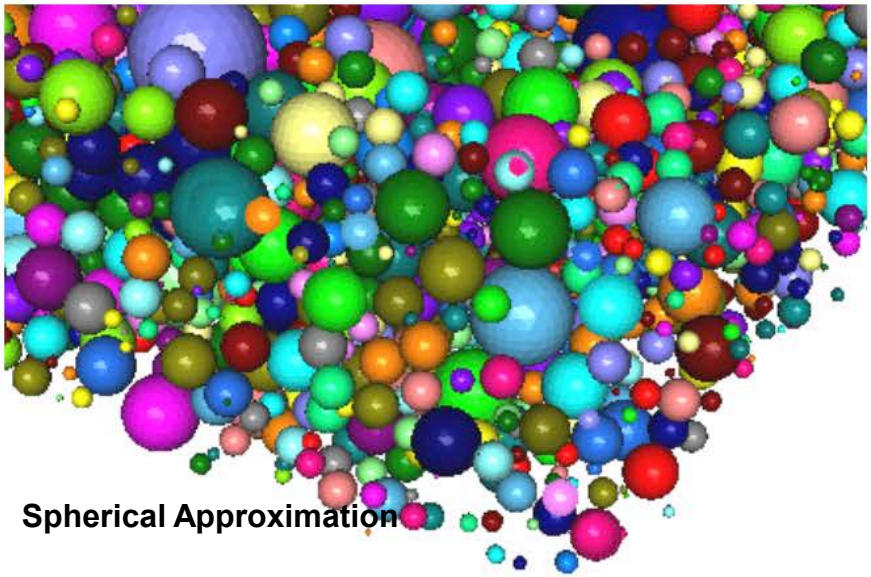
Models for Electrode Microstructure



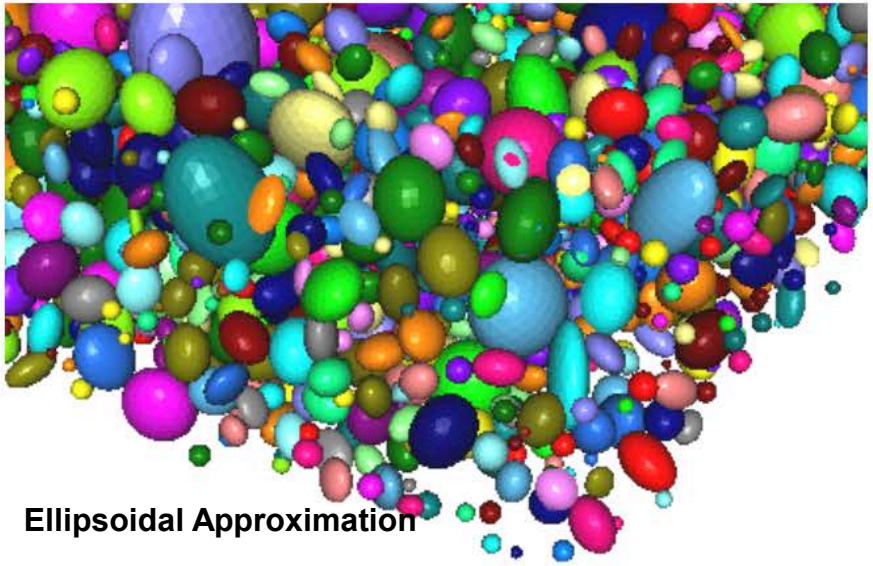
Raw Tomography



Meshed Particles



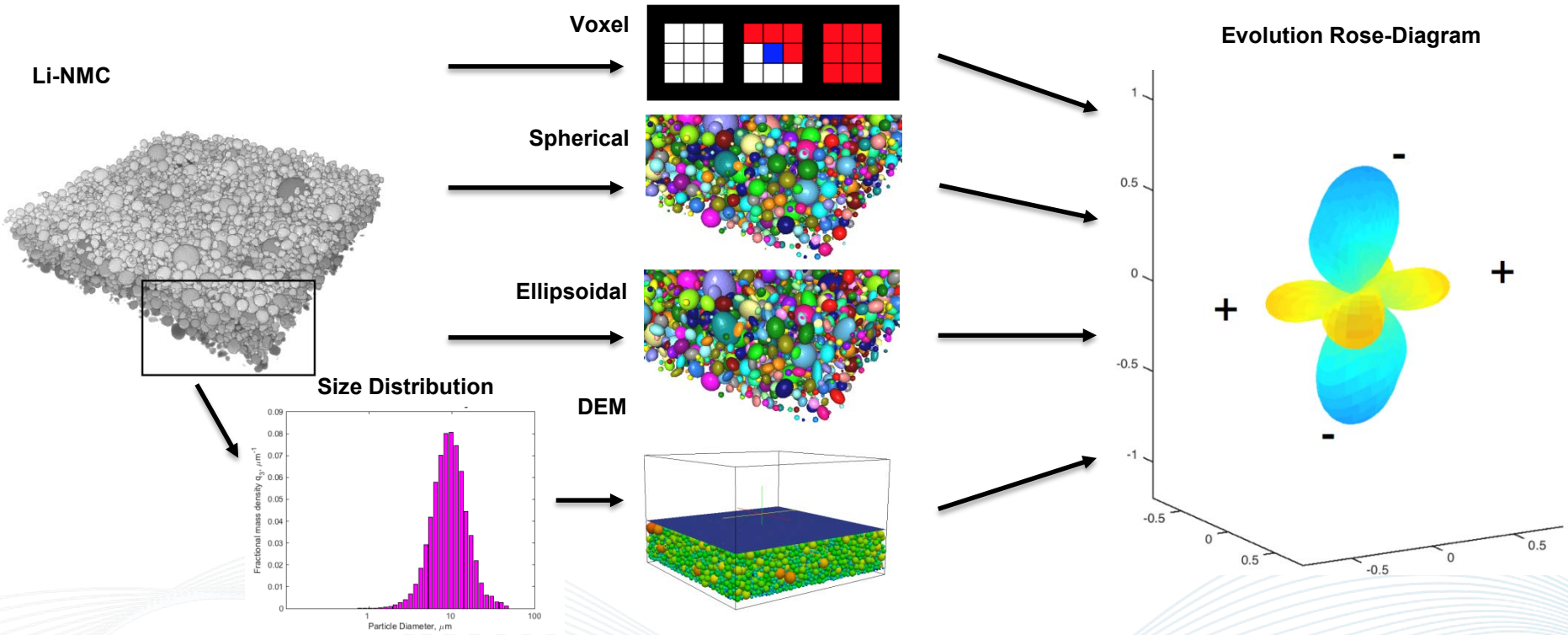
Spherical Approximation



Ellipsoidal Approximation

Fabric Tensor Formulation

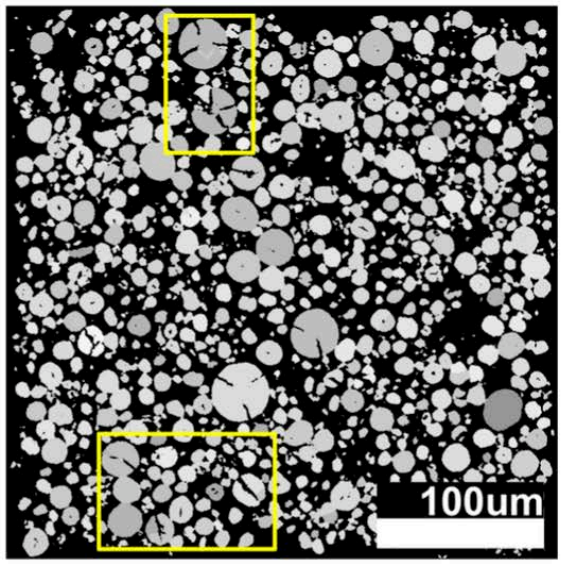
- Use established methods and models from mechanics of saturated granular materials and bonded porous aggregates.
  - Same methods are used to describe damage in materials.
- Clear physical interpretation and relation to experiments.



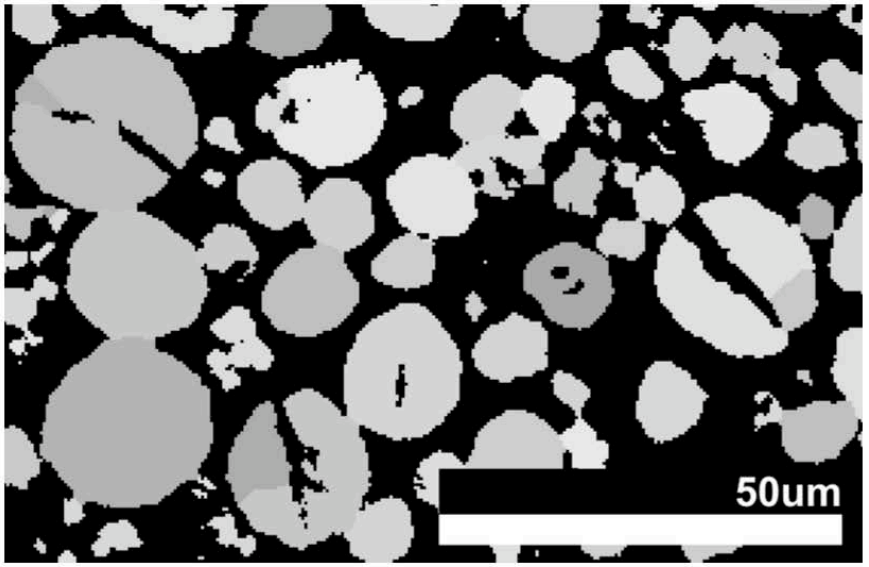
A.J. Stershic, S. Simunovic, J. Nanda, J. Power Sources 297 (2015) 540-550

Fracturing of the Particles at High Calendaring Pressures

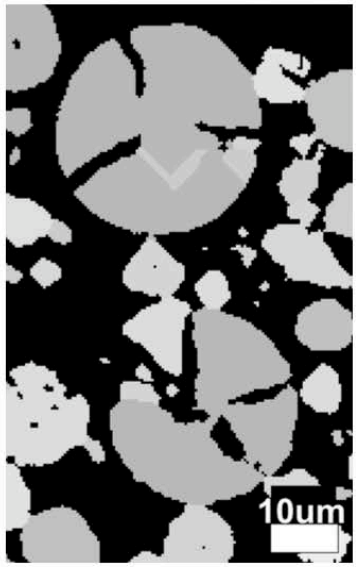
- Particle contact and interaction changes with fracture
- Fabric tensor captures evolution of contact with particle breakage



Top View with selections

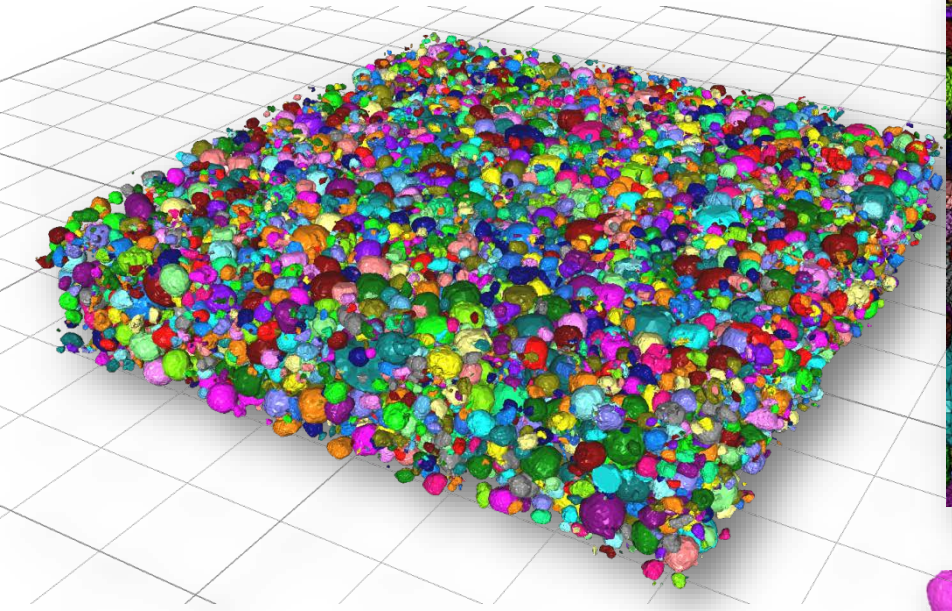


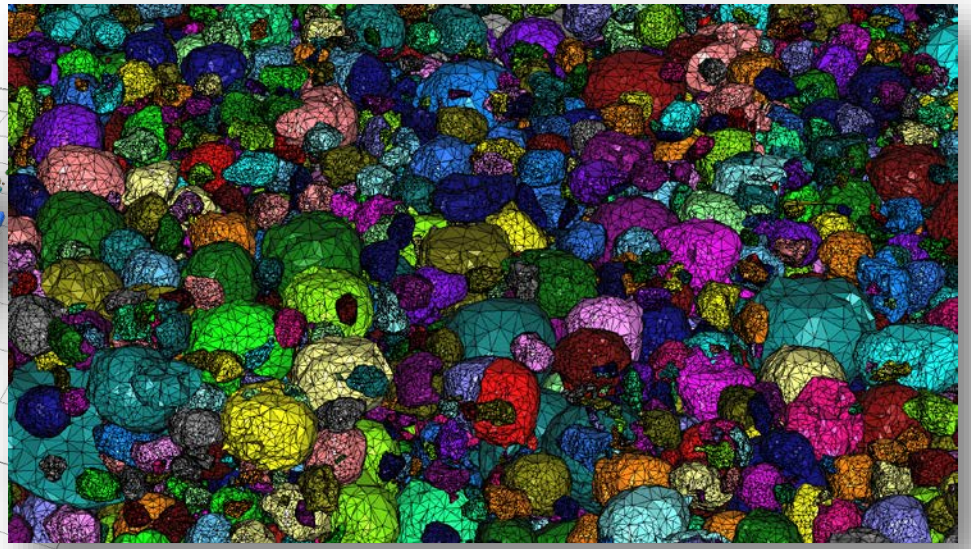
Lower Selection



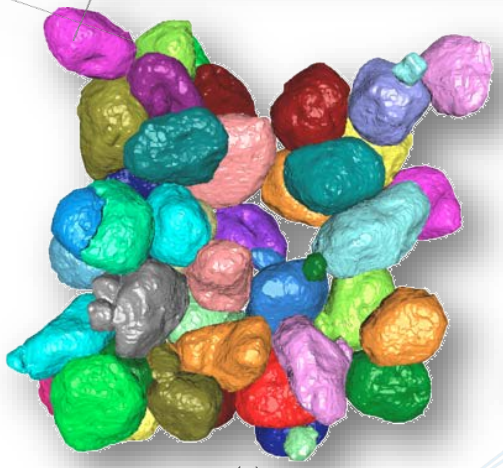
Upper Selection

Mechanical Models for Electrode Materials with Particle Fracture

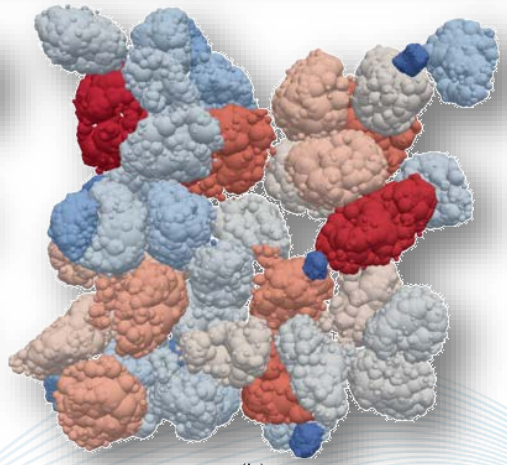




- Upscaling of microstructure simulations using FT formulations
- We are investigating FT methods for upscaling other battery processes and their coupling



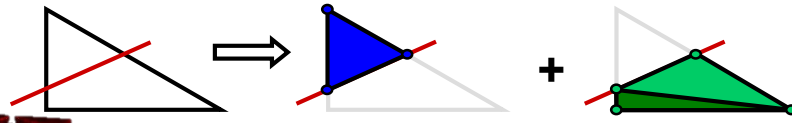
(a)

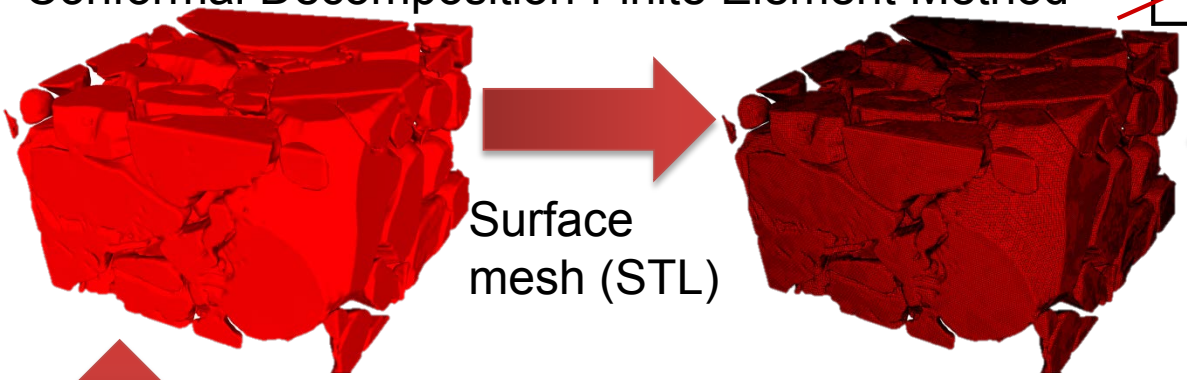


(b)

Conformal meshing of complex microstructures

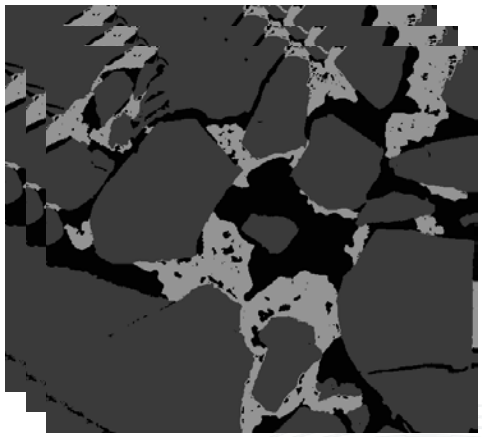
Conformal Decomposition Finite Element Method



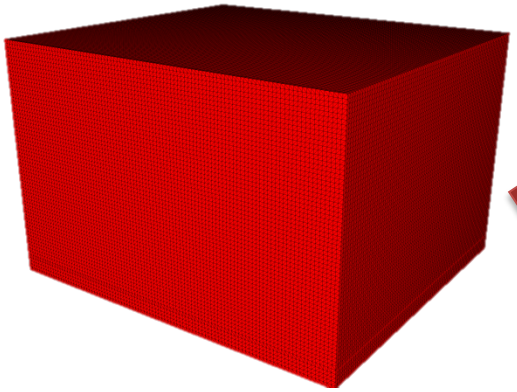


Surface mesh (STL)

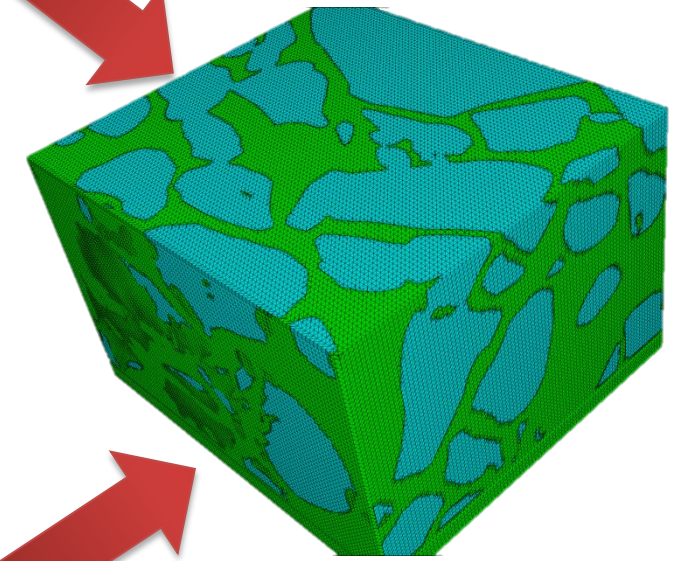
3D reconstruction



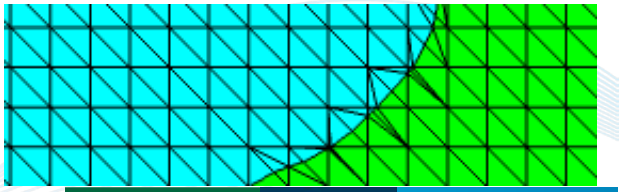
2D image stack



Background mesh



Decomposition of background mesh using CDFEM



Hutzenlaub (2012); Noble (2010); **Roberts (2014)**

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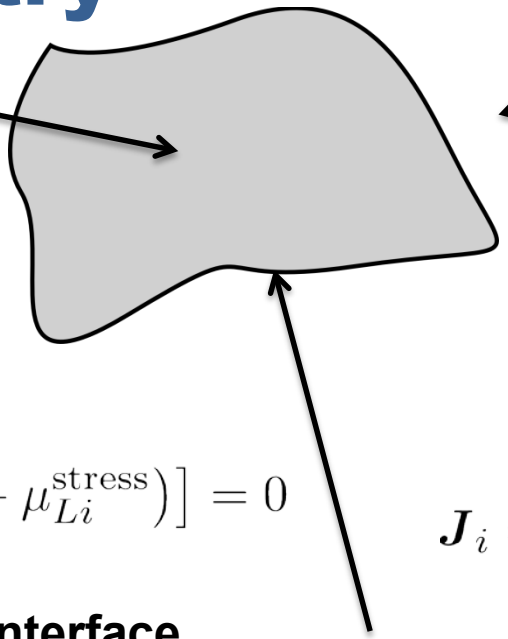
Mathematical model for electrochemistry



In the particle

- Ohm's Law

$$\nabla \cdot (\sigma \nabla \phi_s) = 0$$

- Intercalated Li conservation

$$\frac{\partial C_{Li}}{\partial t} + \nabla \cdot \left[M C_{Li} \nabla \left(\mu_{Li}^{\text{chem}} + \mu_{Li}^{\text{stress}} \right) \right] = 0$$

In the electrolyte

- Current conservation

$$\nabla \cdot \left[F \left(\boldsymbol{J}_{Li^+} - \boldsymbol{J}_{PF_6^-} \right) \right] = 0$$

- Nernst-Planck fluxes

$$\boldsymbol{J}_i = -D_i \left(z_i C_i \frac{F}{RT} \nabla \phi_l + \nabla C_i \right)$$

- Li+ conservation

$$\frac{\partial C_{Li^+}}{\partial t} + \nabla \cdot \boldsymbol{J}_{Li^+} = 0$$

- Electroneutrality

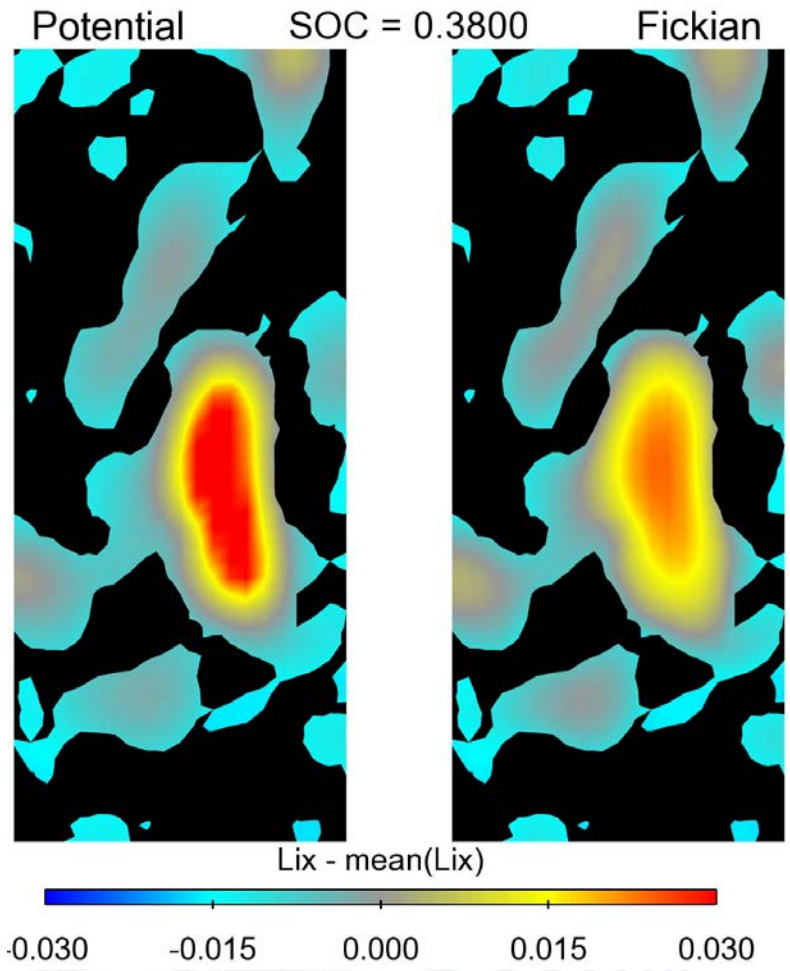
$$C_{PF_6^-} = C_{Li^+}$$

At the interface

- Butler-Volmer reaction rate

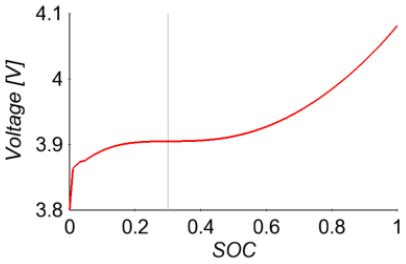
$$\boldsymbol{J} \cdot \boldsymbol{n} - j_0 \left[\exp\left(\frac{\alpha_a F (\phi_s - \phi_l - \phi_{eq})}{RT} \right) - \exp\left(\frac{-\alpha_c F (\phi_s - \phi_l - \phi_{eq})}{RT} \right) \right]$$

Electrochemical behavior with non-ideal lithium transport



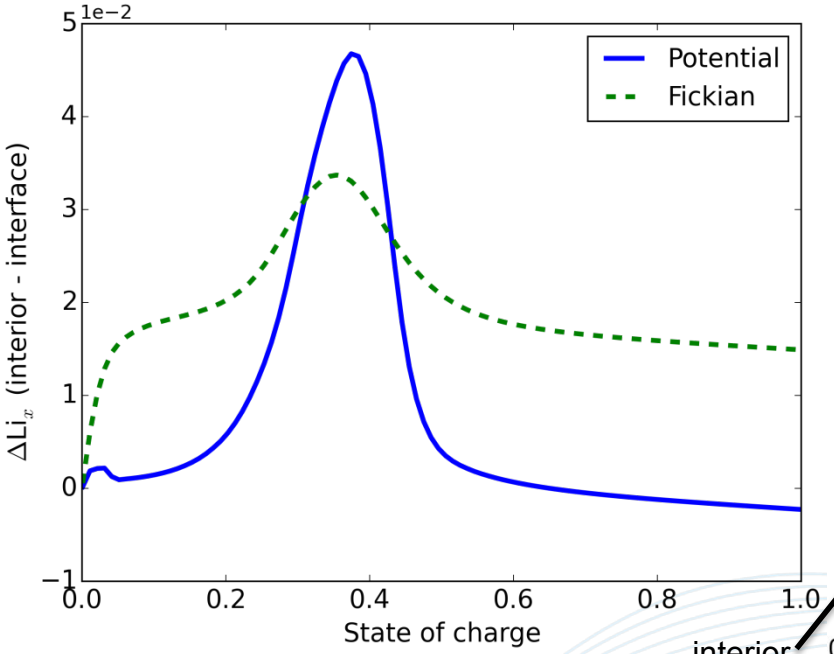
- Ideal transport (Fickian) mod

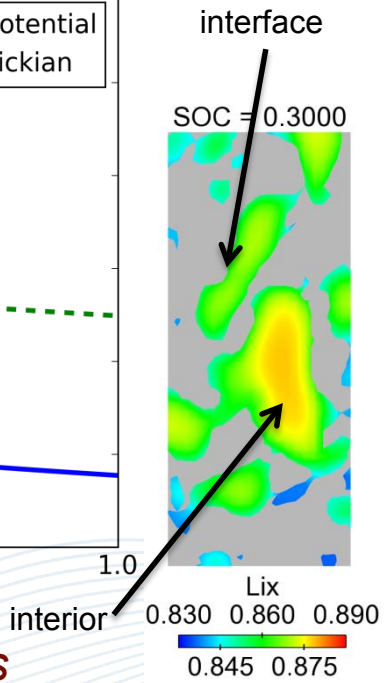
$$\underline{J}_{\mathrm{Li}} = -D\underline{\nabla}C_{\mathrm{Li}}$$



- Non-ideal (potential) model:

$$\underline{J}_{\mathrm{Li}} = -MC_{\mathrm{Li}}\underline{\nabla}\mu_{\mathrm{Li}}^{\mathrm{chem}}$$





Ideal transport model shows unrealistically high concentration gradients

Mendoza, Roberts, et al. (submitted)

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Mathematical model for mechanics

- Intercalation-induced swelling causes a volumetric strain

$$\begin{aligned} \boldsymbol{E} &= \boldsymbol{E}_{\text{elastic}} + \boldsymbol{E}_{\text{swelling}} \\ &= \boldsymbol{E}_{\text{elastic}} + \boldsymbol{\alpha}\Delta C_{\text{Li}} \end{aligned}$$

- For a linear elastic constitutive behavior, swelling is converted to stress
  - Analogous to standard "coefficient of thermal expansion" approach

$$\begin{aligned} \boldsymbol{\sigma} &= \boldsymbol{C} : \boldsymbol{E}_{\text{elastic}} \\ &= \boldsymbol{C} : \boldsymbol{E} - \boldsymbol{C} : \boldsymbol{\alpha}\Delta C_{Li} \\ &= \boldsymbol{C} : \boldsymbol{E} - \boldsymbol{\beta}\Delta C_{Li} \end{aligned}$$

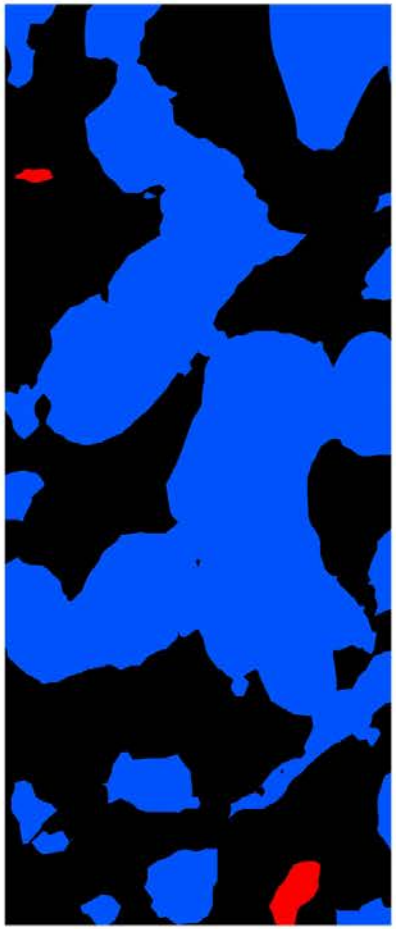
- Generally, volumetric strain is isotropic

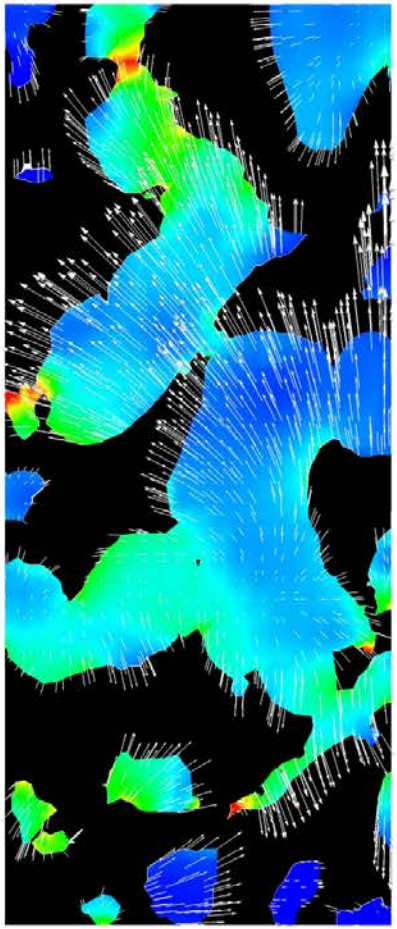
$$\boldsymbol{\beta} = \beta\boldsymbol{\delta}$$

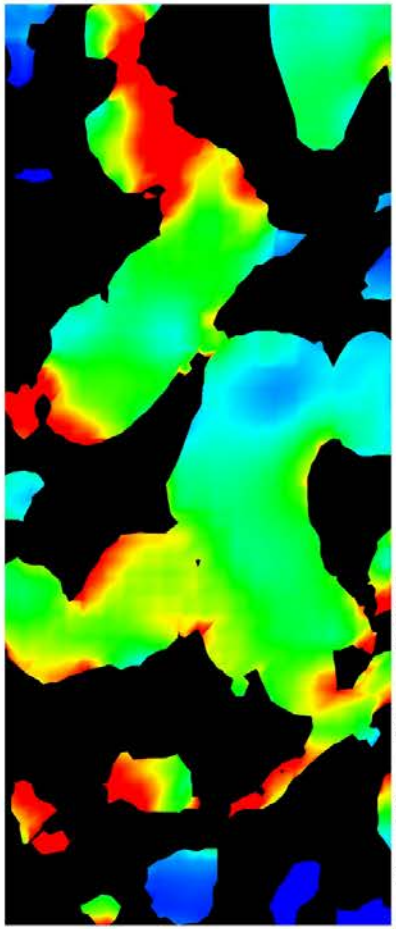
- Stress governed by quasi-static momentum conservation

$$\boldsymbol{\nabla} \cdot \boldsymbol{\sigma} + \boldsymbol{F} = \boldsymbol{0}$$

Stress development in LCO network







Lix

0.500 0.625 0.750 0.875 1.000

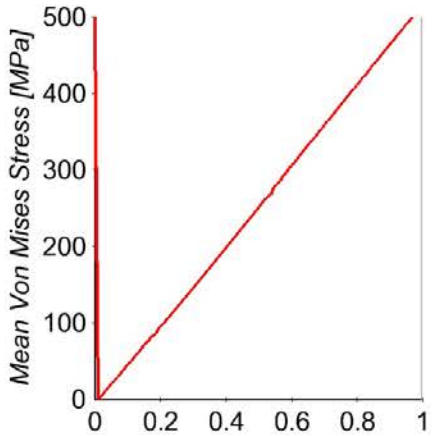
Equivalent Strain

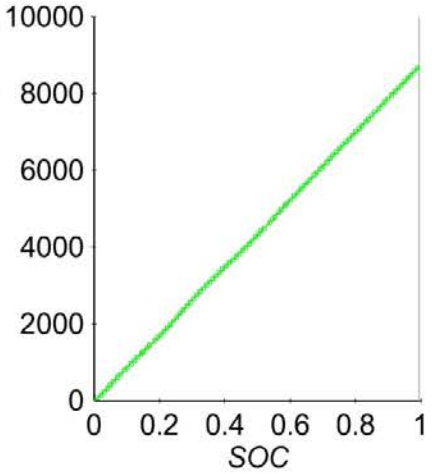
0.000 0.001 0.002 0.004 0.005

Von Mises Stress [MPa]

0 250 500 750 1000

SOC = 0.995





Particle confinement leads to 100x higher stresses than in isolated particles

Mendoza, Roberts, et al. (submitted)

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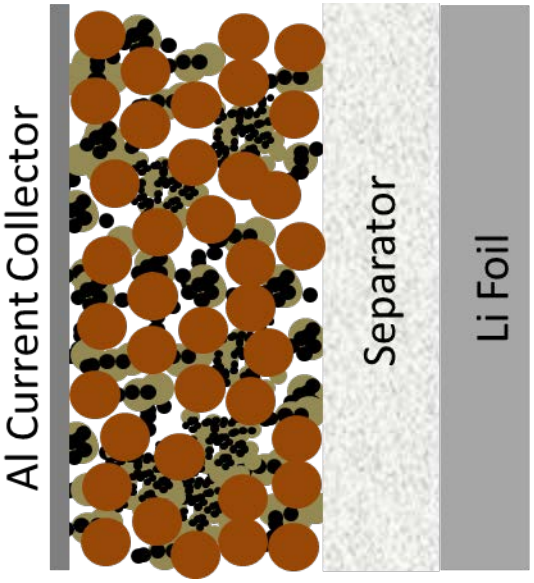
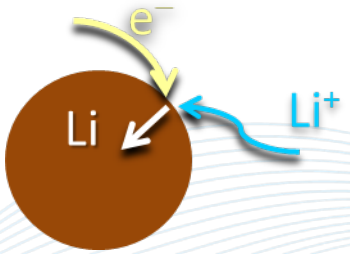
Srinivasan group core strength: battery model development

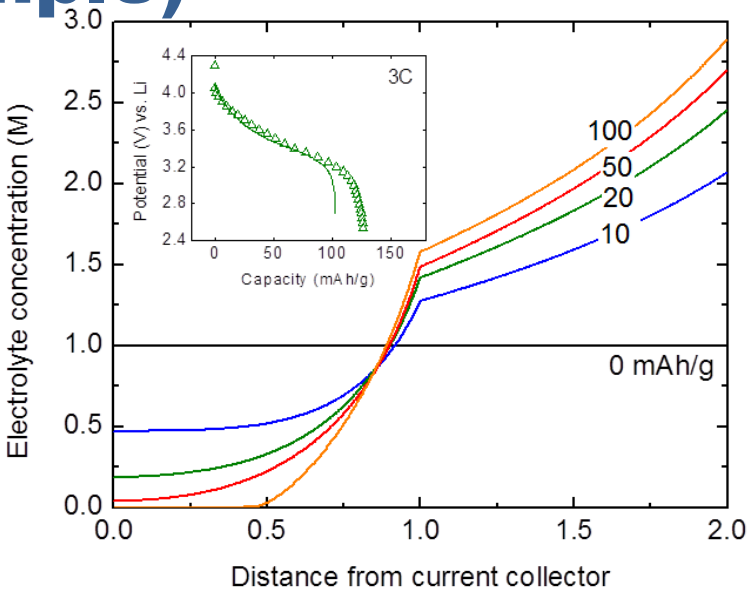
- Building on Prof. John Newman's work on porous electrodes
- Spatially-averaged equations & parameters, simple geometries
- Qualitative understanding at low computational cost
- Past work on LFP, NMC, graphite; currently building Li-S model

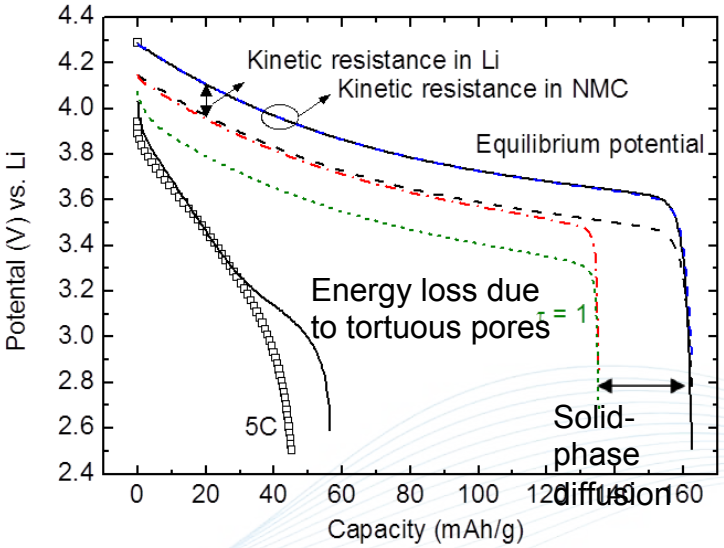




Macroscale models provide insight into performance (NMC example)

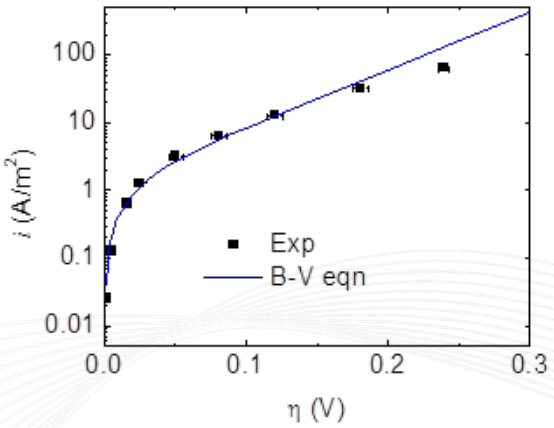
- Rapidly provide predictions of spatial variation
- Allows examination of capacity limitations
- Allows exploration of potential drops and capacity loss mechanisms

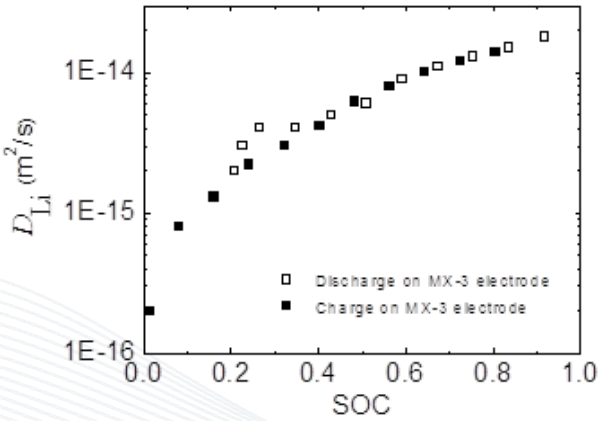


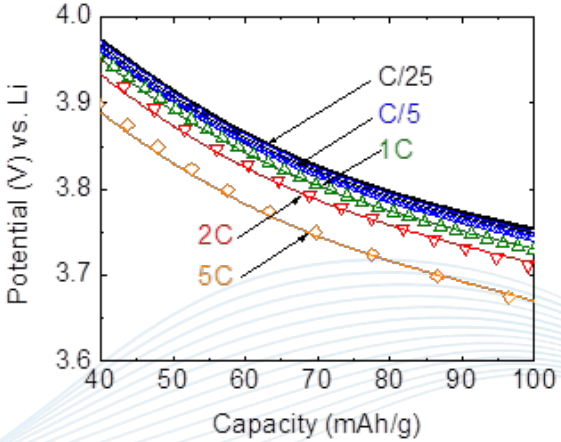


Systematic experiments provide model parameters (NMC example)

- Li surface reaction kinetics from low-current experiments with Li-Li symmetric cell
- DLi(SOC) in NMC from open-circuit relaxation experiments with thin electrode, single particle model
- NMC surface reaction kinetics from rate experiments with thin electrode, single particle model







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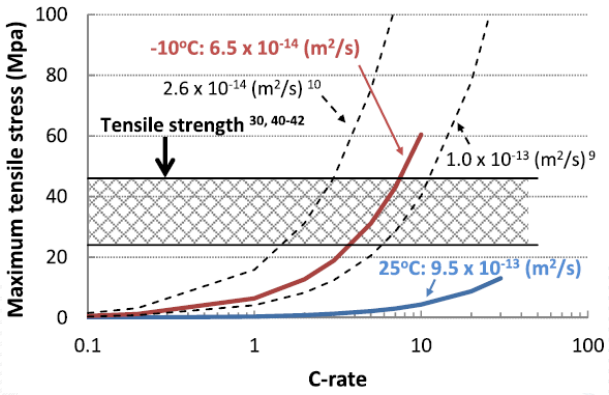
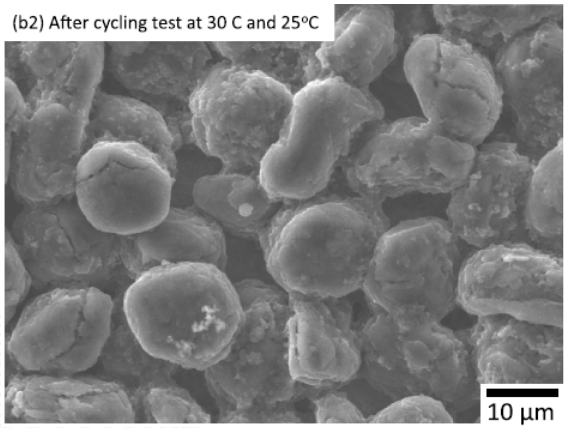
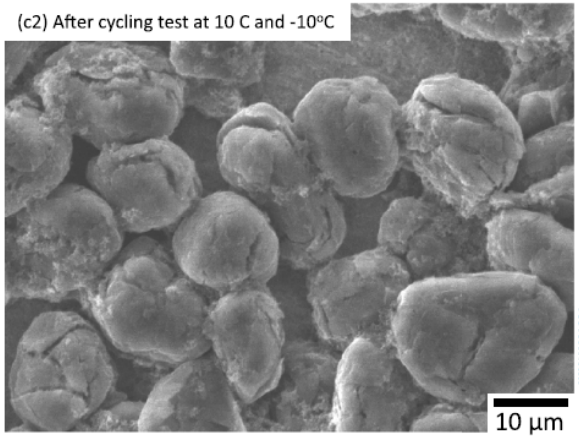
Mechanical simulations consider other performance limitations (graphite)

- Single particle diffusion-induced stress model investigates particle cracking
- Diffusivity of Li in graphite at two temperatures from thin electrode experiments, single-particle model
- SEM images after cycling tests show damaged and undamaged particles consistent with model results







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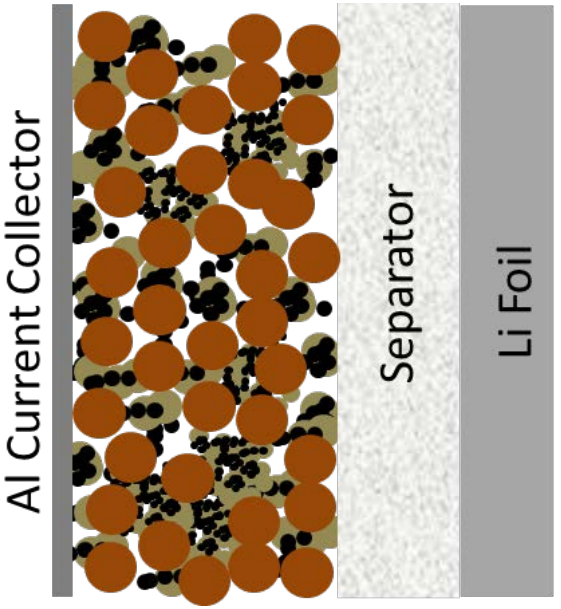
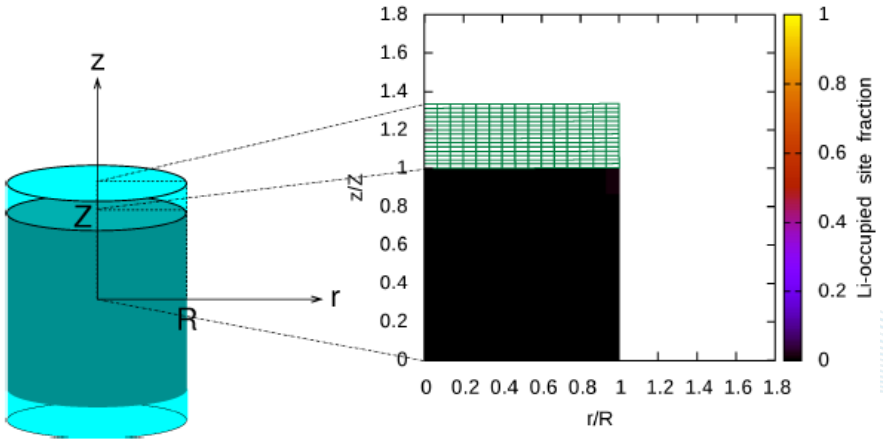
Expanded mechanical simulations consider interaction with binder

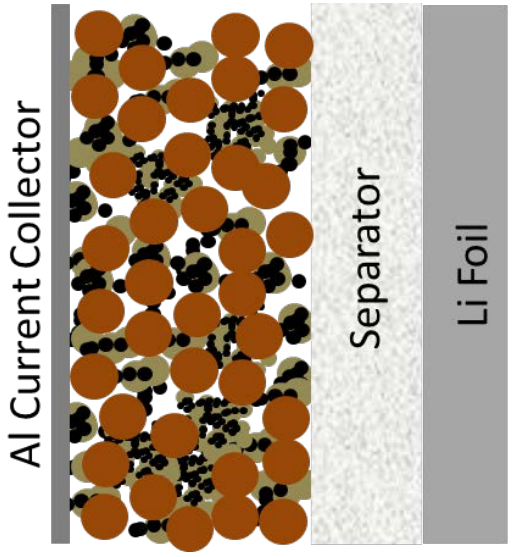
- Active material particles attached to surrounding material
- Silicon shows 300% expansion, fully lithiated
- Large-deformation mechanics, built on work by Christensen and Newman
- Axisymmetric model system: particle with attached binder

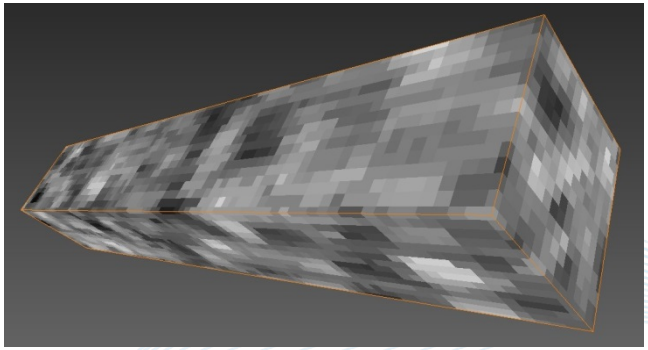




Realistic electrode geometries might improve model accuracy

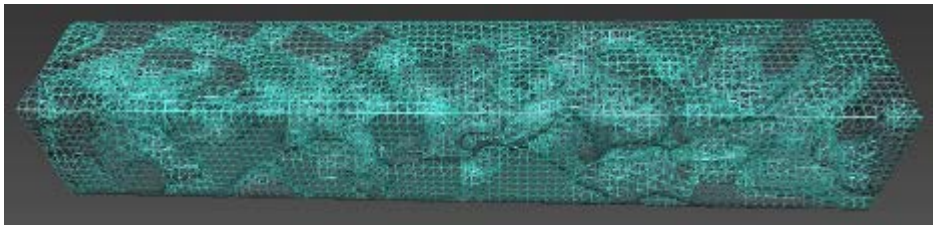
- What is the cost of spatial averaging?
- Using X-ray microtomography at ALS to obtain electrode reconstructions
- Yields intensity in 3D region divided into volume elements ("voxels")
- "Segmentation" of voxels according to phase



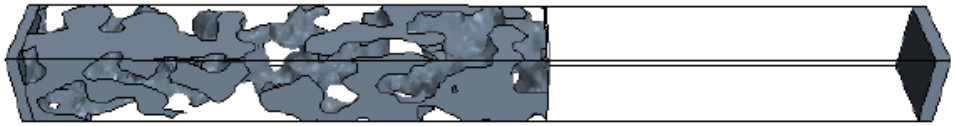


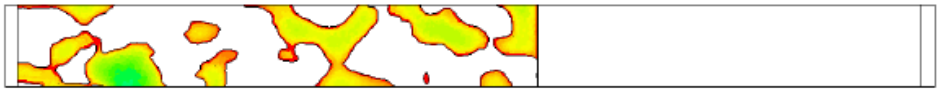
Developed workflow from sample preparation to microscale simulation

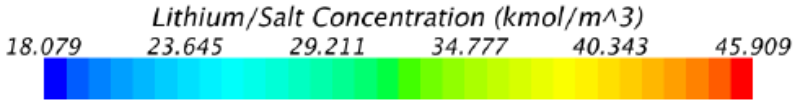
- Reconstructions turned into surface meshes
- Governing equations without spatial averaging
- Fine detail with high computational cost
- How different from macroscale simulation, and why?

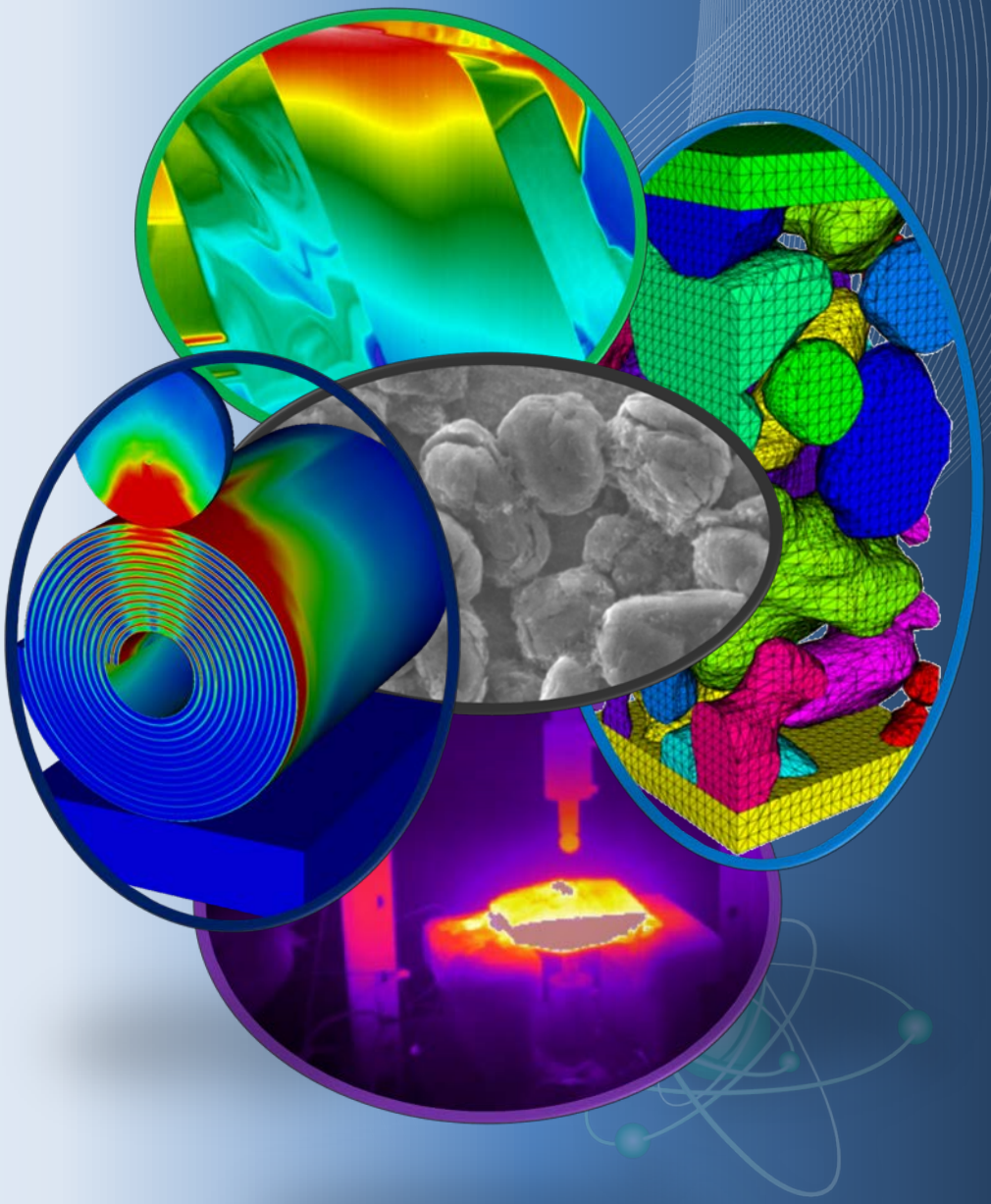


10 μm x 10 μm x 57 μm sample









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